CANADIAN JOURNAL OF RESEARCH

VOLUME 26 FEBRUARY, 1948 NUMBER 2

— SECTION B —

CHEMICAL SCIENCES

Contents

Page

The Composition of Aluminium Stearate—*Wilfred Gallay and Ira E. Puddington* - - - - - - - - - - - - 155

Kinetic Studies on Methyl-bis-β-chloroethylamine. I. The Hydrolysis of the Piperazinium Dimer—*A. L. Thompson, T. J. Hardwick, A. W. Hay, and C. A. Winkler* - - - - - 161

Kinetic Studies on Methyl-bis-β-chloroethylamine. II. The Kinetics of the Action of Sodium Thiosulphate on the Piperazinium Dimer—*A. L. Thompson, T. J. Hardwick, and C. A. Winkler* - - - - - - - - - - - - - 170

Kinetic Studies on Methyl-bis-β-chloroethylamine. III. The Kinetics of the Dimerization in Methanol—*A. W. Hay, A. L. Thompson, and C. A. Winkler* - - - - - - - - - 175

Kinetic Studies on Methyl-bis-β-chloroethylamine. IV. The Kinetics of Dimerization in Aqueous Acetone—*A. L. Thompson, T. J. Hardwick, and C. A. Winkler* - - - - - 181

Kinetic Studies on Methyl-bis-β-chloroethylamine. V. The Reactions in Various Acid Solutions—*T. J. Hardwick, A. L. Thompson, and C. A. Winkler* - - - - - - - - - - 193

Low Temperature, Low Pressure Fractionation. Natural Gas —*E. H. Boomer, A. Gillies, and J. T. Hugill* - - - - - - 202

A Rheological Study of Solutions of Nitrocellulose—*David Fensom and J. H. Greenblatt* - - - - - - - - - - 215

Une Synthèse de la *dl*-Méthionine—*Roger Gaudry et Guy Nadeau* 226

The Effect of Temperature and Mixed Solvent Composition on the Intrinsic Viscosity of GR-S—*L. H. Cragg and T. M. Rogers* 230

The Structure of some Diels-Alder Addition Products—*H. L. Holmes, K. Alcock, D. G. Demianiw, J. W. Robinson, C. E. S. Rooney, and F. A. Sundberg* - - - - - - - - - - 248

NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA

CANADIAN JOURNAL OF RESEARCH

The *Canadian Journal of Research* is issued in six sections, as follows:

A. Physical Sciences	D. Zoological Sciences
B. Chemical Sciences	E. Medical Sciences
C. Botanical Sciences	F. Technology

For the present, Sections A, C, D, and E are to be issued six times annually, and Sections B and F, twelve times annually, each under separate cover, with separate pagination.

The *Canadian Journal of Research* is published by the National Research Council of Canada under authority of the Chairman of the Committee of the Privy Council on Scientific and Industrial Research. The *Canadian Journal of Research* is edited by a joint Editorial Board consisting of members of the National Research Council of Canada, the Royal Society of Canada, and the Chemical Institute of Canada.

Sections B and F of the *Canadian Journal of Research* have been chosen by the Chemical Institute of Canada as its medium of publication for scientific papers.

EDITORIAL BOARD

Representing NATIONAL RESEARCH COUNCIL	*Representing* ROYAL SOCIETY OF CANADA	
DR. A. R. GORDON, (*Chairman*), Head, Department of Chemistry, University of Toronto, Toronto.	DR. A. NORMAN SHAW, Chairman, Department of Physics McGill University, Montreal.	Section III
DR. C. H. BEST, The Banting and Best Department of Medical Research, University of Toronto, Toronto.	DR. J. W. T. SPINKS, Department of Chemistry, University of Saskatchewan, Saskatoon.	
DR. ROBERT NEWTON, President, University of Alberta, Edmonton, Alta.	DR. E. HORNE CRAIGIE, Department of Zoology, University of Toronto, Toronto.	Section V
DR. G. H. HENDERSON, Professor of Mathematical Physics, Dalhousie University, Halifax.	DR. H. S. JACKSON, Head, Department of Botany, University of Toronto, Toronto.	

Ex officio	*Representing* THE CHEMICAL INSTITUTE OF CANADA
DR. LÉO MARION, Editor-in-Chief, Division of Chemistry, National Research Laboratories, Ottawa.	DR. R. V. V. NICHOLLS, Associate Professor of Chemistry, McGill University, Montreal.
DR. H. H. SAUNDERSON, Director, Division of Information Services, National Research Laboratories, Ottawa.	

EDITORIAL COMMITTEE

Editor-in-Chief,	DR. LÉO MARION	Editor, Section D,	DR. E. HORNE CRAIGIE
Editor, Section A,	DR. A. NORMAN SHAW	Editor, Section E,	DR. J. B. COLLIP
Editor, Section B,	DR. J. W. T. SPINKS DR. R. V. V. NICHOLLS	Editor, Section F,	DR. J. A. ANDERSON DR. R. V. V. NICHOLLS DR. A. NORMAN SHAW
Editor, Section C,	DR. H. S. JACKSON		

Manuscripts should be addressed:

Editor-in-Chief,
Canadian Journal of Research,
National Research Council, Ottawa, Canada.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 26, SEC. B. FEBRUARY, 1948 NUMBER 2

THE COMPOSITION OF ALUMINIUM STEARATE[1]

BY WILFRED GALLAY AND IRA E. PUDDINGTON

Abstract

The composition of aluminium stearate as normally prepared approximates that of the distearate. Extraction over extended periods, using ethyl alcohol, acetone, and methyl ethyl ketone as extractants, reduced the proportion of stearic acid to that of a monobasic soap. Excess stearic acid over that represented by the monostearate is adsorbed and removable by solvent extraction. In the presence of moisture, extensive hydrolysis occurs, leading to a large excess of alumina. The results obtained by solvent extraction are corroborated by the indicator titration and electrometric titration experiments. It is concluded that aluminium stearate is monobasic only, and that neither the distearate nor the tristearate exists.

Aluminium soaps, such as aluminium stearate, are widely used for industrial purposes and in various laboratory investigations. Aluminium stearate is sold commercially in several 'forms', e.g., as the mono-, di-, and tristearate, or under code letters designating these supposed compounds. It is widely recognized that the properties of this soap depend on the proportion of fatty acid contained, and, that in the preparation of the soap, close adherence to a standard procedure must be maintained in order to obtain the same results in various applications. The factors that influence the composition of aluminium stearate have been described (1), and the ease of hydrolysis of the soap in an aqueous medium has been shown (2).

Several workers have shown that tribasic aluminium soaps are nonexistent (2, 3, 4). For the soaps used in their work on dipolar moments and structural viscosity, Ostwald and Riedel (5) report compositions ranging from 1.88 to 2.73 moles of stearic acid per mole of aluminium. These were prepared by the usual double decomposition method, and the products were washed with alcohol and ether. Compositions of aluminium stearate represented by these proportions are typical of the soaps prepared in this way. McBain and McClatchie (4) have reported the composition of aluminium soaps prepared by various means. By double decomposition in an aqueous medium, the aluminium stearates prepared by them contained from 5.0 to 6.2% aluminium. The theoretical aluminium content is as follows: mono-, 8.3%; di-, 4.4%; tri-, 3.1%. It is apparent therefore that the gross composition was somewhat nearer to dibasic than to monobasic soap. In nonaqueous media, similar results were obtained. After extraction with dry ether, the aluminium

[1] *Manuscript received June 26, 1944.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1688.

palmitates prepared by McBain and McClatchie contained about 5.3% aluminium (theoretical for dibasic soap is 4.9% and for monobasic soap is 9.1%). McBain and McClatchie conclude that aluminium soaps are commonly a mixture of uncombined free fatty acid with either a monobasic or a mixture of mono- and dibasic soaps.

The present work presents further evidence on the composition of aluminium stearate.

Composition

The composition of a number of aluminium stearates, prepared as follows, was investigated,

1. A commercial soap 'C', termed a 'distearate'.
2. Soap 'C', extracted in a Soxhlet overnight with petrolic ether.
3. Soap prepared by reacting potassium stearate with aluminium sulphate in aqueous solution. The product was washed with cold water and dried.
4. Soap prepared by double decomposition as in No. 3. The product was washed with cold water and then extracted with petrolic ether.
5. Soap prepared by double decomposition as in No. 3. The product was washed with hot water and dried.
6. Soap prepared by double decomposition as in No. 3. The product was washed with hot water and then extracted with petrolic ether.
7. Activated aluminium metal and stearic acid were refluxed for four hours in xylene. The solvent was evaporated off, and the product was extracted with petrolic ether. The metal was activated with mercuric chloride in methyl alcohol solution.
8. Soap prepared as in No. 7. The product was heated in boiling water prior to extraction with petrolic ether.

Table I shows the analyses of these soaps in metallic content, as represented by aluminium oxide.

TABLE I

COMPOSITION OF ALUMINIUM STEARATES

No.	Al_2O_3, %	No.	Al_2O_3, %
1	7.8	5	7.2
2	9.1	6	9.8
3	7.3	7	7.8
4	9.7	8	9.1

It is noted that these data may be divided roughly into two groups, viz., (1) the extracted soaps, in which the aluminium oxide content is 9.1 to 9.8%, and (2) the unextracted soaps, which have an aluminium oxide content of 7.2 to 7.8%. Table II shows the corresponding composition for the theoretical soaps of various basicities.

It is apparent that the composition of the soaps shown in Table I corresponds approximately to the distearate. It might be assumed from the above that the extracted soaps are mixtures of mono- and distearates, chiefly the latter, and this corresponds to the conclusions of previous workers noted above.

TABLE II

COMPOSITIONS OF THEORETICAL ALUMINIUM STEARATES

Soap	Calc. % Al_2O_3
Aluminium tristearate $Al(C_{18}H_{35}O_2)_3$	5.8
Aluminium distearate $Al(OH)(C_{18}H_{35}O_2)_2$	8.4
Aluminium monostearate $AlO(C_{18}H_{35}O_2)$	15.6

Extraction

Further investigation was then carried out on a more extended extraction of aluminium stearates with several solvents for fatty acids. It is apparent that fatty acid removable by solvent extraction is uncombined, and attempts were made to reach equilibrium values in proportion of metal to fatty acid. The soaps used were Mallinckrodt's technical aluminium stearates. On analysis they showed the following:

	Al_2O_3, %
Tristearate	6.98
Distearate	8.83
Monostearate	14.55

Extractions were carried out in a Soxhlet apparatus under one of two general conditions, viz., (1) ordinary conditions, i.e., the solvent was not carefully dried, and no provisions were made for the exclusion of moisture, and (2) the solvent was carefully dried prior to use, alkali was used in the receiver, and the condenser was fitted with a drying tube. After a given period of extraction, the soap was analysed and the basicity expressed in the form of per cent aluminium oxide.

It is noted that where water was not carefully excluded, fatty acid was continuously extracted far beyond the theoretical for the monostearate. It would appear, therefore, that small quantities of water effect a hydrolysis of the monostearate to a complex binary of aluminium hydroxide and stearic acid. The tristearate yields a large proportion of stearic acid within a short time, indicating that a part of the stearic acid is relatively loosely bound, as compared with the distearate.

Where water was excluded, however, the composition of the soaps reached approximately the theoretical for the monostearate within seven days' (or less) extraction, and remained virtually unchanged after an additional six days' extraction.

TABLE III

ETHYL ALCOHOL EXTRACTION

Soap	Extraction period, days	Moisture conditions	% Al_2O_3 in extracted soap
Distearate	0.75	Moist	9.7
"	2	"	12.7
"	2.75	"	16.5
"	9	"	19.3
"	15	"	21.3
Tristearate	0.75	"	13.8
Distearate	7	Dry	15.8
"	13	"	15.6

As in ethanol extraction experiments, the data in Table IV show the hydrolytic effects of water on the soap. Where water was excluded, the composition had a value close to the theoretical for the monostearate, and this value

TABLE IV

ACETONE EXTRACTION

Soap	Extraction period, days*	Moisture conditions	% Al_2O_3 in extracted soap
Distearate	3	Moist	9.7
"	5	"	10.1
"	6	"	12.4
"	9	"	14.2
"	9 + 6	"	23.0
"	3 + 1	"	10.8
"	3 + 1 + 1.25	"	13.2
"	3 + 1 + 1.25 + 2	"	18.3
Monostearate	1	"	15.3
Tristearate	0.75	"	10.7
"	0.75	"	9.8
Distearate	11	Dry	12.7
"	11 + 9	"	15.0
"	28	"	16.0

* *Successive figures denote additional extraction periods preceded by drying.*

remained essentially unchanged (within experimental error) after an additional eight days' extraction. It is noted that where the original soap was the monostearate, very little extraction could be effected within 24 hr.

The unrefined methyl ethyl ketone used in the first two extractions shown in Table V contained appreciable titratable acidity, and was used in the five-

TABLE V

METHYL ETHYL KETONE EXTRACTION

Soap	Extraction period, days	Moisture conditions	% Al_2O_3 in extracted soap
Distearate	1	Moist	13.0
"	5	"	31.8
"	4	Dry	11.9
"	11	"	14.4
"	28	"	16.4

day extraction in an extractor of a type that freely admitted the entrance of much moisture to this system. The result was a very considerable hydrolysis with very large excess of alumina in the extracted soap.

Where moisture was excluded, the composition reached that of the theoretical monostearate after lengthy extraction; this was similar to results obtained with other solvents.

Titration

Further experiments were carried out using a titration method to determine the fatty acid adsorbed but not combined.

A sample of the technical distearate was titrated with $N/10$ sodium hydroxide in an acetone–alcohol medium using phenolphthalein as indicator. The end point, which was not very well defined, was taken at the point where the pink color remained stable for a period of two minutes. In two experiments, the results obtained agreed approximately with the composition aluminium monostearate + stearic acid for the technical distearate. A similar titration using the technical tristearate agreed very closely with the composition aluminium monostearate + 2 (stearic acid).

In view of the fact that the end points of these titrations were not altogether satisfactory, an electrometric titration of the technical tristearate was carried out, using again $N/10$ sodium hydroxide in an acetone–alcohol medium. The pH meter was of the portable glass electrode type. Two color indicators were added also, viz., (1) a mixture of phenol red and brom thymol red, indicating normally a change at pH 7.5, and (2) phenolphthalein, indicating normally a change at pH 9. The results are shown in Fig. 1, where the pH is plotted against the quantity of alkali added. The curve shows two inflections in the regions where the two indicators change color. The fact that these are somewhat higher than the theoretical values for the 'di-' and 'mono-' soaps may be accounted for by assuming the presence of fatty acids of lower molecular weight in the technical 'tristearate'. It is noted that the color changes occur at pH values considerably higher than those normally obtained in aqueous solution. Titration of stearic acid against $N/10$ sodium hydroxide

in acetone–alcohol medium, with the indicators used above, showed that the actual transitions were in fact at pH 9.5 and 10.3 for the mixed indicator and phenolphthalein respectively.

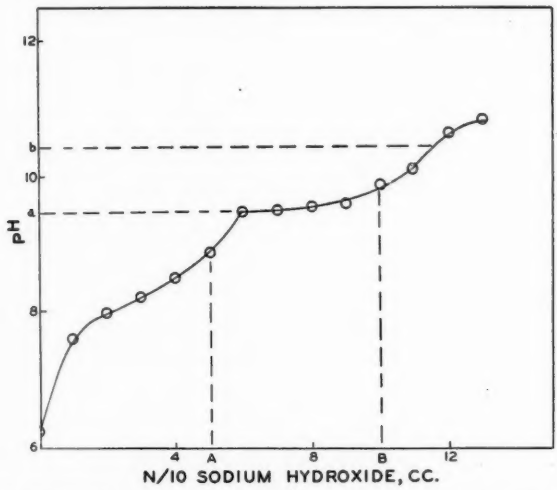


FIG. 1. *Potentiometric titration of aluminium stearate. A and B; theoretical end points for the distearate and tristearate respectively;* a, *actual end point for mixed indicator and* b, *actual end point for phenolphthalein.*

Acknowledgment

This work was carried out under an arrangement between the Imperial Oil Limited and the National Research Council of Canada.

The authors wish to express their thanks to Imperial Oil Limited for permission to publish this paper.

References

1. CORNIL, R. Ing. chim. 22 : 1. 1938.
2. EIGENBERGER, E. and EIGENBERGER-BITTNER, A. Kolloid-Z. 91 : 287. 1940.
3. LICATA, F. J. Drugs, Oils & Paints, 51 : 148, 150. 1936.
4. MCBAIN, J. W. and MCCLATCHIE, W. L. J. Am. Chem. Soc. 54 : 3266. 1932.
5. OSTWALD, Wo. and RIEDEL, R. Kolloid-Z. 69 : 185. 1934.

KINETIC STUDIES ON METHYL-BIS-β-CHLOROETHYLAMINE

I. THE HYDROLYSIS OF THE PIPERAZINIUM DIMER[1]

A. L. THOMPSON,[2] T. J. HARDWICK,[3] A. W. HAY,[4] AND C. A. WINKLER

Abstract

The literature on the chemistry of methyl-bis-β-chloroethylamine is reviewed. The hydrolysis of the dimer is shown to proceed through a unimolecular mechanism whose rate expression is given by $k = 1.0 \times 10^{14} e^{-29400/RT}$ hr.$^{-1}$. Secondary processes of higher activation energy are observed.

Introduction

Methyl-bis-β-chloroethylamine has certain physiological effects which at one time indicated that it might be useful as an agent in Chemical Warfare. Since stabilization of the compound presented a problem, a series of investigations was made in this laboratory on the kinetics of the degradation process under various conditions. These included studies in methanol, aqueous acetone, and various dilute acids as solvents for the methyl-bis-β-chloroethylamine. Hydrolysis of the piperazinium dimer and its reaction with sodium thiosulphate were also investigated. Throughout this and subsequent papers methyl-bis-β-chloroethylamine will be represented by 'S'. To orientate the several problems involved, a review of the literature relevant to the several papers to be submitted is included in this first paper of the series.

'S' is one of several nitrogen analogues of mustard gas. Freshly distilled it is a colorless, oily liquid with a marked tendency to supercool, for although the melting point of the solid is −63° C., the liquid is frozen with difficulty at −78° C. The vapor pressure of 'S' is given by the formula (9)

$$\log_{10} P = 7.045 - 2259/T$$

The amine is soluble in water only to the extent of 1.2% at room temperatures (7) but is miscible with several organic solvents.

Pure 'S' on standing at room temperature over a period of time deposits a fluffy mass of small white crystals, the rate of formation of which increases with an increase in temperature or when a solvent such as methanol or ethanol is present.

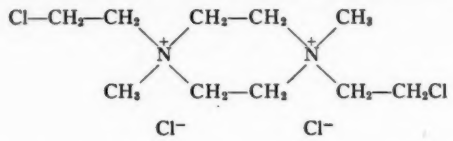
[1] *Manuscript received in original form February 17, 1947, and, as revised, November 17, 1947. Contribution from the Physical Chemical Laboratory, McGill University, Montreal, with financial assistance from the National Research Council. The work reported in this and subsequent papers of the series was done during the years 1942–1944.*

[2] *Holder of a studentship under the National Research Council of Canada. Present address: Radiation Laboratory, McGill University.*

[3] *Holder of a Studentship under the National Research Council of Canada. Present address: National Research Council, Chalk River Laboratory.*

[4] *Holder of a Studentship under the National Research Council of Canada. Present address: Canadian Industries Ltd., Central Laboratory, McMasterville, Que.*

Evidence that the precipitate formed in 'S' has the structure



arises from molecular weight determinations by the isopiestic method (1), chemical analysis of the dimer and its dipicrate, m.p. 208° C. (14), and from measurements of its ionizable chlorine. Hanby and Rydon (8) have confirmed the structure by direct comparison with synthetic material.

Burns, Eastwood, and McAlpine (2) examined the stabilizing effect of a number of substances on 'S'. Antioxidants in general were found to promote dimerization. Among organic solvents, chlorobenzene, carbon tetrachloride, chloroform, and dioxane had a decided stabilizing effect, their ability decreasing in the order listed.

Briscoe (1) found that compounds containing a hydroxyl group, whether acid, phenol or alcohol, have a marked accelerating influence.

Marion (14), in agreement with Burns, Eastwood, and McAlpine (2), found that hydroquinone had an accelerating effect. Ammonium chloride apparently caused no change in the rate of solid formation, while thiourea appeared to have possibilities as a stabilizer.

All experimental results on stabilization mentioned previously were obtained by measuring the amount of solid produced in the liquid 'S', a method which obviously neglects the possibility of reaction to form soluble products. However, any reaction which 'S' might undergo, such as hydrolysis, dimerization, iminization, etc., produces chloride ion and analysis for this ion should give a more reliable estimate of the amount of 'S' reacted.

From the work cited above it appears that nonionizing solvents act as stabilizing agents, while polar solvents, particularly hydroxy compounds, usually act as catalysts for the polymerization of pure 'S'. However, owing to the doubtful accuracy of the analytical procedure, the relative merits of the various stabilizing agents mentioned cannot be reliably judged.

In hydrochloric acid solution, 'S' forms a stable hydrochloride, 'S'–HCl. This is obtained as a white solid by precipitation with acetone, from which it may be recrystallized (m.p. 110° C.). In the dry state the hydrochloride is very stable and provides a convenient form in which to store 'S'.

Question has been raised concerning the stability of the hydrochloride in water. Robinson (19) followed the production of chloride ion with acidified silver nitrate. He found 19.25% of the total chlorine ionizable in 72 hr. at room temperature. Sandin and Nichol (20) reported 1% hydrolysis in two days at 24° C. and 40% at 90° C. in 10 min. Marion, using sodium hydroxide and silver nitrate to measure hydrogen ion and chloride ion production, found 1.3% hydrolysis in 20 days and 3.4% in 47 days. However, Marion (14)

points out that there may be an error in these results, since varying the coagulation time for silver chloride varied the amount of chloride ion analyzed.

Robinson (19) suggested that in water an equilibrium

$$\text{'S'} + \text{HCl} \rightleftarrows \text{'S'H}^+ + \text{Cl}^-$$

exists. In such a case one or more of the following reactions may be anticipated.

(*a*) Hydrolysis of 'S'H$^+$ ion,
(*b*) Hydrolysis of 'S',
(*c*) Dimerization of 'S',
(*d*) Formation of a stable imine from 'S'.

Robinson (19) also studied the hydrolysis of 'S'–HCl in a solution which was 3 *N* with respect to sodium hydroxide. The hydrochloride, and subsequently the 'S', decomposed at a very rapid rate. Those results are in agreement with those of Sandin and Nichol (20) who studied the reaction of 'S'–HCl in 7.5 *N* ammonium hydroxide. However, no reaction product other than chloride ion was determined in this work.

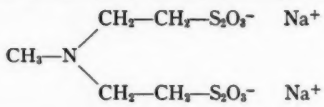
A characteristic reaction of 'S' is its behavior in water. Dixon (4) made conductivity measurements during the reaction of 0.001 *M* 'S' in 30% alcohol – 70% water solution. The conductivity increased and approached a constant value in six minutes. Chloride ion production was followed by precipitation with acidified silver nitrate. No hydrogen ion production occurred at first, but small amounts appeared as time progressed. He reported that the conductivity value reached was about what would be expected if one chlorine per molecule of 'S' became ionic. From his results he considered the reaction to be dimerization followed by hydrolysis of the dimer.

Young, Miller, and Hopewell (22) followed the production of chloride ion in the two phase system 'S'–water. Only 50% of the total chlorine present was found in the ionizable state. The rate increased on stirring the two phases. The investigators concluded that dimerization was the main reaction of 'S' in water. They also followed the effect of pH on the rate of production of chloride ion in 'S'–water mixtures and concluded that 'S' in water is stabilized at pH 3.5 or less, forms dimer (or higher polymer) at pH values between 4 and 7, and that the dimer undergoes hydrolysis above pH 8.

Ogston (16) followed the formation of hydrogen and chloride ions in 5% ethanol – 95% water at 25° C. over a large range of pH. Chloride ion analysis was made by titrating excess silver nitrate with potassium thiocyanate. Hydrogen ion was measured by titrating the whole solution with small portions of 0.1 *N* sodium hydroxide and measuring the time required for the pH to reach a definite value (indicators). The rate of chloride ion production was the same at pH 6 to 8 as at pH 9 to 10. The relative rates of hydrogen ion and chloride ion production at various pH values were:

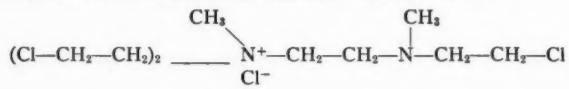
pH	Rate of H^+/rate of Cl^-
9 – 10	0.016
6.5 – 7	0.067
4.5 – 5	About 1.0

In sodium thiosulphate solution, chloride ion formation was found to be independent of thiosulphate ion concentration, although chloride ion was replaced by thiosulphate ion mole for mole forming a compound



At low pH, direct hydrolysis occurred. At pH 5 to 10 hydrolysis was the main reaction, complicated, however, by slight dimerization. The hydrogen ion production did not equal the chloride ion formation since 'S'–chlorohydrin and 'S'–diol formed by hydrolysis were much stronger bases than 'S' and removed hydrogen ion from solution, so that it was not detected by the analytical method used. At pH 12 the concentration of ions is so great that hydrolysis is the only possible reaction.

Further extensive work was done on the reaction of 'S' in water solution by Hanby *et al.* (7). Since only half of the available chlorine was liberated at a rate equal to the disappearance of 'S', these investigators were of the opinion that hydrolysis of the β-chlorines occurs, liberating hydrogen ion, which neutralizes the remaining 'S' and prevents further hydrolytic action. They assumed the formation of an ethylene–imine ring which is broken by hydrolysis to give 'S'–chlorohydrin or hydrochloric acid to generate 'S'H^+. When the quaternary 'S'H^+ ion is formed the negative β-chlorine atoms are bound more closely to the positive nucleus than in the free amine. Iminization is impossible in the quaternary 'S'H^+ state. The initial rate of chloride ion production was the same in 1% solution as in 0.01% solution of 'S'. In 1% solution 95% of the 'S' disappeared while weak base hydroxyl compounds were present to the extent of only 7% as found by the base titre from pH 3.8 to 11. The authors admitted the existence of the piperazinium dimer in the reaction products, but considered a possible product to be:



which would not undergo ring closure to cyclic dimer.

This compound may undergo further polymerization by the formation of the imine ring and subsequent reaction with more 'S'. This mechanism agrees with that postulated by Jones and coworkers (11) for the polymerization of β-chloroethylamine. However, no evidence of any long chain polymer has ever been reported.

Conductivity measurements by Hanby *et al.* (7) showed that the equivalent conductance of 'S' on standing 60 min. at 25° C. in water is 113 at 0.00067 molar and 92 at 0.064 molar initial concentration of 'S', while dimer under the same conditions had equivalent conductances of 120 and 80 respectively. This greater difference with pure dimer was taken as evidence that dimer was present only in small quantities in the 'S' solution.

Hanby and Rydon (9) heated 'S' in evacuated bulbs and found the deposition of a white precipitate to occur. If the space above the 'S' in the bulbs were filled with water vapor, the appearance of the solid, identified as dimer by its picrate, was more rapid. Carbon dioxide-free air caused the appearance of a rust-colored precipitate, as did pure oxygen. The authors believed that water catalyzes dimer formation, while oxygen reacts with 'S' to give rust-colored products and water, which cause precipitation of dimer. The production of chloride ion was studied at 100°, 132°, and 154° C. From initial rates the energy of activation of the reaction, which was concluded to be dimerization, was estimated as 20.0 kcal.

Thus while Robinson (19), Dixon (4), and Young, Miller, and Hopewell (22) were of the opinion that the main course of the reaction is dimerization followed by dimer hydrolysis, Ogston (16) and Hanby, Hartley, Powell, and Rydon (7) concluded the main reaction to be the hydrolysis of 'S' which is complicated by dimerization and the formation of quaternary products such as imines. The fundamental difference of opinion was the relative rates at which hydrolysis and dimerization of 'S' take place. These investigators also disagreed on the effect of pH on the reaction rate.

In view of the confusion indicated above and in view of the apparent complexity of the reactions of 'S'–HCl in aqueous solution, it was decided to study the kinetics of the formation of chloride and hydrogen ions in solutions of 'S' in methanol and aqueous acetone and solutions of $'SH^+$ in water. Before this could be done on a reasonably sound basis, stability of the dimer had first to be determined, so that any necessary corrections for the production of hydrogen and chloride ions by dimer hydrolysis might be applied when measurements of dimer formation were made.

Experimental

A. *Materials*

The 'S' was obtained in the form of the crude hydrochloride from the National Research Council, Ottawa*. The 'S'–HCl was purified by repeated crystallization from water. The purified hydrochloride was dissolved in cold water and neutralized with ammonium hydroxide while kept cool. Cold benzene was added and the 'S' extracted into the upper layer. The excess benzene was distilled off and the remaining concentrate of 'S' was redistilled.

The 'S' dimer used in the investigation was prepared by allowing a 1 *M* solution of 'S' in absolute methanol to react at 25° C. for several days. The product was filtered and washed repeatedly with acetone. It was then recrystallized from methanol–acetone (1 : 1), washed with dry acetone and finally dried at 100° C. for several days. Analysis for ionizable chlorine gave the theoretical amount (2 equivalents of Cl^- per mole dimer of molecular weight 312).

* *We are very grateful to Dr. L. Marion, of the National Research Laboratories, Ottawa, for the generous supplies of this material made available to us for all the studies reported in this series.*

Stock solutions were prepared by dissolving a weighed amount of dimer in water at 25° C. Aliquot portions were pipetted into Pyrex bulbs which were subsequently sealed. These bulbs were heated for measured times in oil baths thermostatically controlled at different temperatures with suitable refluxing liquids.

B. *Analytical Procedure*

The contents of a bulb was diluted with distilled water and titrated with standard sodium hydroxide (carbonate free) to the initial pH of 4.8 (Beckman pH meter) to obtain a measure of the hydrogen ion production. The solution was then made more alkaline (pH 6 to 7) and an argentometric determination for chloride ion made, using potassium chromate as indicator. A blank on the chloride ion content was obtained by analysis of an aliquot of the original dimer solution.

Experimental Results

Representative experimental data are presented in Table I. The quantity of 'S' dimer taken for each sample was 0.500 millimole. When the reaction is complete the theoretical value for base titre and chloride ion production should be 1.000 millimole. The rate of hydrolysis is calculated throughout from chloride ion production, employing the usual relation:

$$k = \frac{2.3}{t} \log_{10} \frac{a}{a - x}.$$

TABLE I

DATA ON THE HYDROLYSIS OF 'S' DIMER IN AQUEOUS SOLUTION

Reaction temperature = 154.5° C.

Time, hr.	Milliequivalents of		k (hr.$^{-1}$) (Cl^- production)
	Base titre	Cl^- produced	
(*a*) *Initial concentration of 'S' dimer = 31.2 gm./liter (0.1 M)*			
2	0.214	0.235	1.33×10^{-1}
4	0.394	0.386	1.22
6	0.523	0.502	1.15
9	0.640	0.630	1.07
17	0.856	0.835	1.06
34.5	1.01	0.922	1.09
35	1.06	0.940	
70	1.13	0.990	
(*b*) *Initial concentration of 'S' dimer = 15.6 gm./liter (0.05 M)*			
2	0.223	0.227	1.29×10^{-1}
4	0.387	0.372	1.16
6	0.548	0.530	1.29
15	0.908	0.824	1.16

The values obtained were reasonably constant throughout the reaction time, particularly for the reaction temperature 131° C. The results are summarized in Table II. The plot of $\log_{10}k$ (average) against $1/T$ gives a good linear relation. The rate expression for the hydrolysis of the dimer becomes:

$$k = 1.0 \times 10^{14}\, e^{-29{,}400/RT}\ \text{hr.}^{-1}.$$

At higher temperatures the simple hydrolysis is complicated by secondary processes as indicated by the base titre exceeding 1.000 millimole. It is very noticeable at temperatures exceeding 200° C.

TABLE II

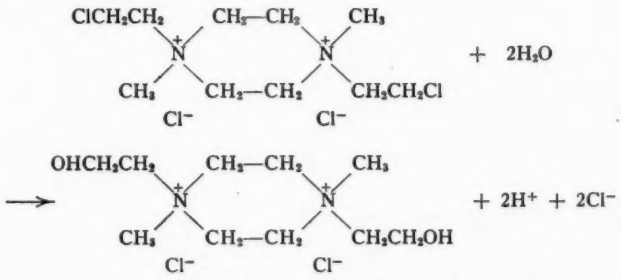
SUMMARY OF AVERAGE FIRST ORDER RATE CONSTANTS FOR THE HYDROLYSIS OF 'S' DIMER IN AQUEOUS SOLUTION AT VARIOUS TEMPERATURES

Initial concentration of 'S' dimer =	0.1 *M*	0.05 *M*
Temperature, °C.	k, hr.$^{-1}$	k, hr.$^{-1}$
131.0	1.77×10^{-2}	—
154.5	1.20×10^{-1}	1.23×10^{-1}
178.0	0.72	0.73

Discussion

The reaction of 'S' dimer in water is rather exceptional in that it involves substitution at a saturated carbon atom which is a constituent of an ion. The structure of the ion involves a six-membered ring with unit positive charges in opposition.

The equation for the hydrolysis follows:



Examination of the data reveals that the process is first order with respect to dimer ion.

The k values appear to fall slightly as reaction proceeds (Table I) simultaneously with a marked increase in hydrogen ion concentration of the solution. The greater change in pH is for the first 15% reaction (or shift from 5 to about 1.5). Increase in chloride ion concentration may also retard the reaction. Preliminary experiments in alkaline solution indicated that hydroxyl ion has an appreciable effect on the rate and course of the hydrolytic process.

The products of such a reaction were usually brownish and were of such a nature as to render inaccurate any analysis similar to the one used in these experiments. Decomposition to lower amines was probably one course of the reaction, as indicated by difficulty in titration and by an amine odor.

The more quantitative investigations of Cohen (3) show that the rate at pH 10 is five times as great as the rate at pH 8; at pH 11, measurement of the rate became difficult.

There are two principal mechanisms possible for the hydrolysis:

(1) An ionization mechanism, or

(2) The direct reaction with water.

The mechanism may be pictured in either of the following ways: (where RCl^{++} represents the dimer ion and the chlorine atoms which undergo substitution are considered individually).

$$(1)\quad RCl^{++} \longrightarrow R^{+++} + Cl^-$$
$$R^{+++} + OH^- \longrightarrow ROH^{++}$$

$$(2)\quad RCl^{++} + H_2O \longrightarrow HOH{-}R^{++}\ldots Cl$$
$$HOH{-}R^{++}\ldots Cl + OH^- \longrightarrow ROH^{++} + H_2O + Cl^-$$

In considering the first, the strength of the C—Cl bond, which according to Pauling (17) is 66.5 kcal., must be kept in mind. Since ionization is the rate governing step in this mechanism the activation energy for the process should be greater than 29.4 kcal., unless perhaps hydration of chloride ion may provide the necessary difference in energy in a manner comparable to that postulated by Hughes (10) for the hydrolysis of *i*-propyl and *t*-butyl chlorides where the activation energy is of the order of 23 kcal. The peculiar structure of dimer ion to which the alkyl chloride in question is attached may account for an increased bond strength.

The occurrence of the second mechanism is rendered improbable by the difficulty of a Walden inversion. The first appears to be the preferred mechanism.

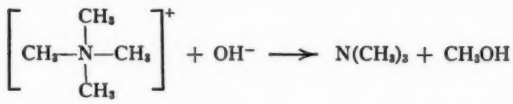
Hanby and Rydon (8) have demonstrated the existence of two stereoisomers of 'S' dimer. No attempt has been made to determine which of the stereoisomeric forms of the dimer was used in the present investigation. It might be of some theoretical interest to determine the relative rates of hydrolysis of the two forms.

An explanation for the excess of base titre over the theoretical presents some difficulty. Some buffering action by the hydrolysis products was observed to render the end point for the base titre at pH 4.8 less definite as the reaction progressed. However, this effect was not sufficiently pronounced to account for the observed increase of hydrogen ion above chloride ion in the later stages.

It might be that a secondary decomposition process with a much higher activation than the hydrolysis reaction gives rise to products with amphoteric properties. This is suggested by a somewhat similar reaction studied by

Graymore (5). By the action of benzyl chloride on cyclic trimethyl trimethylene-triamine he obtained the quaternary compound dibenzyl dimethyl ammonium chloride. Subsequent hydrolysis to produce tertiary and secondary amines showed that it was possible to break the ring quite readily.

Further evidence for the occurrence of a decomposition which produced hydrogen ion and weak bases is obtainable from a discussion by Hammett (6, pp. 144 and 167) on the decomposition of two quaternary ammonium hydroxides. These reactions are known to occur quite readily.



$$(C_6H_5)_2\,CHN_3(CH_3)_3 + OH^- \longrightarrow (C_6H_5)_2\,CHOH + N(CH_3)_3$$

It is quite conceivable that the cyclic structure of the dimer ion offers greater steric hindrance to the removal of a CH_3 group and hence a much higher temperature is necessary.

References

1. Briscoe, H. T. Private communication.
2. Burns, J. W., Eastwood, A., and McAlpine, J. Private communication.
3. Cohen, B. Private communication.
4. Dixon, M. Private communication.
5. Graymore, J. J. Chem. Soc. 39. 1941.
6. Hammett, L. P. Physical organic chemistry; reaction rates, equilibria, and mechanisms. 1st ed. McGraw-Hill Book Co., Inc., New York and London. 1940.
7. Hanby, W. E., Hartley, G. S., Powell, E. O., and Rydon, H. N. J. Chem. Soc. 519. 1947.
8. Hanby, W. E. and Rydon, H. N. J. Chem. Soc. 833. 1945.
9. Hanby, W. E. and Rydon, H. N. J. Chem. Soc. 513. 1947.
10. Hughes, E. D. Trans. Faraday Soc. 34 : 185. 1938.
11. Jones, G. D., Longsjoen, A., Neumann, Sister M. M. C., and Zomlefer, J. J. Org. Chem. 9 : 125. 1944.
12. Knorr, L., Hörlein, H., and Roth, P. Ber. 38 : 3136. 1905.
13. Knorr, L. and Roth, P. Ber. 39 : 1420. 1906.
14. Marion, L. Private communication.
15. Mason, J. P. and Block, H. W. J. Am. Chem. Soc. 62 : 1443. 1940.
16. Ogston, A. G. Private communication.
17. Pauling, L. The nature of the chemical bond and the structure of molecules and crystals; an introduction to modern structural chemistry. Cornell Univ. Press, Ithaca, N.Y., and H. Milford at the Oxford Univ. Press, London. 1939.
18. Prelog, V. and Stepán, V. Collection Czechoslov. Chem. Commun. 7 : 93. 1935.
19. Robinson, D. Private communication.
20. Sandin, R. B. and Nichol, C. Private communication.
21. Sheffer, H. Private communication.
22. Young, J. W., Miller, D. N., and Hopewell, W. W. Private communication.

The authors wish to acknowledge the assistance of the Defence Research Board in procuring the information referred to as 'Private communication'.

KINETIC STUDIES ON METHYL-BIS-β-CHLOROETHYLAMINE

II. THE KINETICS OF THE ACTION OF SODIUM THIOSULPHATE ON THE PIPERAZINIUM DIMER[1]

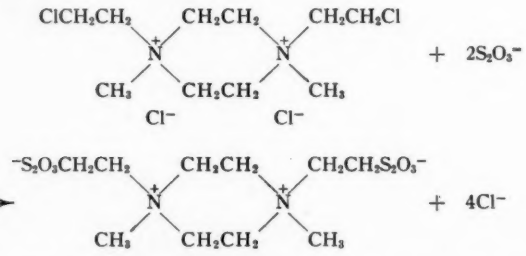
By A. L. Thompson[2], T. J. Hardwick[3], and C. A. Winkler

Abstract

It has been shown analytically that for this reaction the formation of Cl^- agrees with $S_2O_3^=$ disappearance. The approximate first order rate-controlling step is postulated to be dependent on an ionization mechanism. The rate expression calculated from initial rate constants is given approximately by $k = 4.0 \times 10^{15} e^{-25,500/RT}$ hr.$^{-1}$.

Introduction

In an attempt to gain more information about the stability of the β-chlorine atoms in the dimer of 'S' (7) the displacement reaction by thiosulphate has been investigated. This type of reaction has been employed by other workers (1–4, 6) to obtain information on the structure and reactivity of various halogen compounds. La Mer and Kamner (3) have used it to relate the properties of halogenated fatty acids. Ogston (4) investigated the reaction of thiosulphate with 'S' in an effort to explain the peculiarities of its reactions in water. All these investigations dealt with substitution in a negatively charged or neutral body. The displacement reaction of the chlorine atom in the dimer ion by thiosulphate is novel in some respects in that substitution occurs in a positively charged body. The process may be formulated by the following equation:



To supplement the kinetic data obtained by following the reaction iodometrically it was desirable to analyse simultaneously for both chloride ion and thiosulphate ion. Naturally this presented several difficulties. However, an improved method based on that of André Petit (5) has been developed.

[1] *Manuscript received in original form February 17, 1947, and, as revised, November 17, 1947. Contribution from the Physical Chemical Laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council.*

[2] *Holder of a Studentship under the National Research Council of Canada. Present address: Radiation Laboratory, McGill University.*

[3] *Holder of a Studentship under the National Research Council of Canada. Present address: National Research Council, Chalk River Laboratory, Chalk River, Ontario.*

Experimental

(a) Materials and Method

The dimer of 'S' used for the investigation was prepared in the same way as the sample for the studies on hydrolysis (7). The source of the thiosulphate was Merck's Reagent Grade sodium thiosulphate hydrate. Stoichiometric equivalents were dissolved in freshly distilled water at room temperatures. Aliquot portions were sealed into Pyrex bulbs for reaction in thermostats.

(b) Analytical Procedure

The reaction was followed by titrating the samples with standard iodine using fresh starch solution as indicator.

Analysis for chloride ion in the presence of thiosulphate was made in the following way. The thiosulphate content of an aliquot of the sample was determined. Another aliquot was diluted with distilled water to about 125 ml. and 0.5 gm. of sodium acetate added. Standard silver nitrate was measured into the flask in excess of that required to precipitate the thiosulphate as silver thiosulphate. The mixture was heated for a few minutes to complete the decomposition; prolonged heating was avoided since there was a tendency to reduction. The following reactions were believed to take place.

$$2Ag^+ + S_2O_3^{=} \longrightarrow Ag_2S_2O_3\downarrow$$

$$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S\downarrow + H_2SO_4$$

The analytical method is dependent on the fact that silver thiosulphate has a lower solubility product than silver chloride. It is readily hydrolyzed to the more insoluble silver sulphide. During the coagulation process by heating there is no danger of further hydrolysis of the dimer since the reaction is very slow at even 120° C. Sodium acetate is added to facilitate the coagulation of colloidal silver sulphide and to prevent the solution from becoming too acid.

The black precipitate of silver sulphide was filtered off, washed with hot water, and the filtrate cooled. The chloride ion determination was completed by titration with standard silver nitrate to the potentiometric end point of a Ag : AgCl electrode (dichlorofluorescein is probably a suitable indicator). The chloride ion content was determined by deducting from the over-all titre the amount of silver nitrate used to precipitate the thiosulphate. The validity of the procedure was demonstrated analytically and the accuracy of the determinations was shown to be 0.5%.

Results

Representative data are presented in Tables I, II, III. The rate of the substitution reaction approximates to first order with respect of formation of chloride ion or disappearance of thiosulphate ion since changing the concentration of both reactants by $2\frac{1}{4}$ times does not cause appreciable change in rate constant. However, in general the observed first order k values steadily decrease during a run. The rate expression calculated from initial constants is given approximately by the expression

$$k = 4.0 \times 10^{15}\, e^{-25,500/RT}\ \text{hr.}^{-1}. \quad \text{(Table IV).}$$

TABLE I

INITIAL CONCENTRATION OF $S_2O_3^=$ = 0.200 *M*
INITIAL CONCENTRATION OF DIMER = 0.100 *M* (3.12 gm. per 100 ml.)
REACTION TEMPERATURE = 72° C.

Time, hr.	% Reaction			k, hr.$^{-1}$
	$S_2O_3^=$ disappeared		Cl^- formed	
	(1st run)	(2nd run)	(2nd run)	
1/2	13.2	14.1		2.83×10^{-1}
1	24.8	28.0	30.0	2.85
2	41.9	45.5	45.6	2.70
4	63.1	64.8	64.8	2.48
7	79.6			
7.5		81.1	77.0	
12	89.5			
15		95.0	92.0	
23		97.7		

TABLE II

INITIAL CONCENTRATION OF $S_2O_3^=$ = 0.200 *M*
INITIAL CONCENTRATION OF DIMER = 0.100 *M*
REACTION TEMPERATURE = 51.5° C.

Time, hr.	% Reaction	k, hr.$^{-1}$
2	5.7	
5	13.4	2.89×10^{-2}
10	25.6	2.95
19	39.4	2.65
30	50.5	2.35

TABLE III

INITIAL CONCENTRATION OF $S_2O_3^=$ = 0.0800 *M*
INITIAL CONCENTRATION OF DIMER = 0.0400 *M*
REACTION TEMPERATURE = 72° C.

Time, hr.	% Reaction	k, hr.$^{-1}$
1	20.3	2.26×10^{-1}
2	37.0	2.31
4	58.0	2.17
8	75.0	1.76

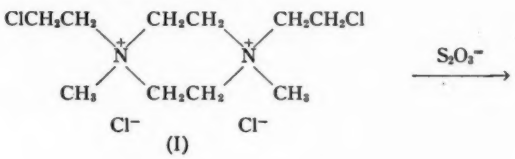
TABLE IV

INITIAL FIRST ORDER RATE CONSTANTS FOR THE REACTION OF 'S' DIMER WITH SODIUM THIOSULPHATE

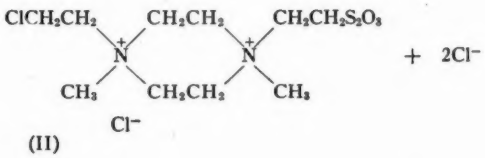
Initial concentration of $S_2O_3^=$ =	0.200 *M*	0.0800 *M*
Initial concentration of dimer =	0.100 *M*	0.0400 *M*
Reaction temperature, °C.	k, hr.$^{-1}$	k, hr.$^{-1}$
85.0	—	12.0×10^{-1}
72.0	3.00×10^{-1}	2.57×10^{-1}
51.5	2.93×10^{-2}	2.57×10^{-2}
35.5	4.2×10^{-3}	

Discussion

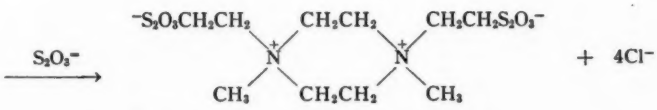
It is quite probable that the reaction between thiosulphate and the dimer ion takes place in two stages, thus:



(I)



(II)



(III)

The second stage may well be different from the first since (II) carries only half the charge of (I). The difference in rate is not readily ascertained. It is to be expected that the final product will be an internally neutralized body.

The approximate first order rate dependence of the process should give further support to the ionization mechanism for displacement reactions at a saturated carbon atom. The rate-controlling step may be assumed to be the polymolecular solvolysis of the chlorine atom to facilitate its removal from the sphere of action.

The difference between the activation energy of the thiosulphate substitution process (25.5 kcal.) and that for hydrolysis (29.4 kcal.), if significant, may be due to the relative solvating strengths of the respective media which will affect the over-all energy barrier of each activated complex in question. The steric factors are approximately of the same order.

It is not improbable that the activation energy for the thiosulphate displacement reaction gives an approximate value for the alkaline hydrolysis for which no direct experimental information is available. However, it might be recalled that Sapozhnikova (6) obtained a value of 15.5 kcal. for the reaction of sodium thiosulphate with sodium monochloroacetate where the activation energy for the alkaline hydrolysis is of the order of 20 kcal. Hence, too much confidence must not be placed in such an interpretation.

References

1. KAPPANNA, A. N. Indian Chem. Soc. 5 : 293. 1928.
2. KAPPANNA, A. N. Indian Chem. Soc. 6 : 45. 1929.
3. LA MER, V. K. and KAMNER, M. E. J. Am. Chem. Soc. 53 : 2832. 1931.
4. OGSTON, A. G. Private communication.
5. PETIT, A. Bull. soc. chim. 51 : 1312. 1932.
6. SAPOZHNIKOVA, N. V. J. Phys. Chem. U.S.S.R. 13 : 174. 1939.
7. THOMPSON, A. L., HARDWICK, T. J., HAY, A. W., and WINKLER, C. A. Can. J. Research, B, 26 : 161. 1948.

The authors wish to acknowledge the assistance of the Defence Research Board in procuring the information referred to as 'Private communication'.

KINETIC STUDIES OF METHYL-BIS-β-CHLOROETHYLAMINE

III. THE KINETICS OF THE DIMERIZATION IN METHANOL[1]

By A. W. Hay,[2] A. L. Thompson[3], and C. A. Winkler

Abstract

The principal reaction of methyl-bis-β-chloroethylamine in methanol is dimerization, which results in one chlorine from each molecule becoming ionic, but this is accompanied by slight alcoholysis. The rate-controlling step is believed to be the first order formation of an ethylenimonium ion which reacts rapidly with one of its kind to form dimer. The rate expression as calculated from initial rate constants is k (initial) $= 4.0 \times 10^{13} e^{-19600/RT} \text{hr.}^{-1}$.

In a previous paper (11), a review has been presented of the literature on the chemistry of methyl-bis-β-chloroethylamine, 'S', that was available when work was commenced in this laboratory. The initial experimental results (11) demonstrated that the dimer is relatively stable compared with 'S'. When this had been established it was possible to follow the course of the dimerization of 'S' in methanol and in aqueous acetone, and to determine the relative extent of dimerization and alcoholysis of 'S' by measurement of chloride ion and hydrogen ion productions respectively.

Experimental

The 'S' was prepared from recrystallized 'S'–HCl by neutralizing it with ammonium hydroxide and extracting with chloroform. The chloroform solution was subjected to a vacuum distillation and the fraction having a boiling point corresponding to that of 'S' was redistilled. The methanol (Merck's Reagent Grade) was dried over calcium oxide for 36 hr., at the end of which time it was distilled over fresh calcium oxide, the boiling point of the final product being 64.5° C.

Stock solutions were prepared by adding precooled methanol to a weighed quantity of 'S' at −78° C. (dry ice – acetone bath). Since no reaction was observed, the pure compound and its solutions were stored at this temperature.

Aliquot portions of these stock solutions were sealed in Pyrex bulbs at −78° C., due allowance being made for expansion of the solution in coming to the reaction temperature. The transfer of solution to these bulbs was made with a pipette connected to a water suction pump through a scratched stopcock. It was necessary to enclose the body of the pipette and the graduated stem in a glass jacket containing calcium chloride to prevent condensation

[1] *Manuscript received in original form February 17, 1947, and, as revised, November 17, 1947.*

Contribution from the Physical Chemical Laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council.

[2] *Holder of a Studentship under the National Research Council of Canada. Present address: Canadian Industries Ltd., Central Research Laboratory, McMasterville, Quebec.*

[3] *Graduate Student and holder of a Studentship under the National Research Council of Canada. Present address: Radiation Laboratory, McGill University, Montreal, Canada.*

of moisture on the walls of the pipette. The smooth surface of the rubber stopper constituting the bottom of the pipette jacket fitted the neck of the stock solution container quite closely, preventing moisture from condensing into the solution. Ice formed on the stem of the pipette while it was draining. To keep this ice from contaminating the stock solution, it was allowed to melt and the stem of the pipette was dried carefully after the transfer of each sample.

A mixture of ice and water was used as a constant temperature bath at 0° C. Other thermostats were controlled to 0.05° C. by the conventional methods with thermoregulators, relays and heating coils.

Although the Volhard method for the determination of chloride ion apparently has been used with success by Ogston (9) the production of chloride ion was followed by precipitation with silver nitrate in 4 *N* nitric acid.

The liquid in a bulb was transferred to a beaker containing approximately 10 ml. of the acid, after which any precipitated dimer was washed out of the bulb into the beaker with separate portions of the acid, the volume of the resulting solution being about 60 ml. After the white precipitate dissolved, 15 ml. of 10% silver nitrate solution was added and the silver chloride precipitate coagulated by heating over a steam bath for one hour. The precipitate was then filtered on a sintered glass crucible, washed with 0.02 *N* nitric acid and with acetone, dried for one hour at 100° C., and weighed. Determinations on solutions of known chloride content in the presence of various concentrations of 'S' indicate the above procedure to give results accurate to 0.0015 gm. of silver chloride.

It was found that if an acidic solution of 'S' was prepared by adding a weighed amount of 'S' to a volume of acid in excess of that required for neutralization of the 'S' then this solution could be titrated with standard base to give two reasonably sharp end points with a Beckman pH meter. The titre to the first end point (pH 3.8) corresponded to the excess of acid. Further titration neutralized the hydrogen ion which was combined with 'S' to form 'S'H^+. This titre to the second end point (pH 8.5) represented the amount of 'S' present. This also applied to the reverse acidic titration from pH 8.5 to 3.8 ('S' + $H^+ \rightarrow$ 'S'H^+). These titres gave results accurate to 1% and formed the basis of the following procedure.

In a reacted sample of 'S' in methanol the hydrogen ion from alcoholysis formed 'S'H^+ and was determined by titration with standard base to pH 8.5. The sample was immediately back titrated with standard acid to pH 3.8 to check the total amount of 'S' left in solution.

Experimental Results

Typical analytical figures obtained in the investigation are given in Tables I, II, III. The figures in the right hand column of these tables are obtained by subtracting the amount of hydrogen ion produced from the amount of chloride ion produced. In all cases complete reaction is represented by the disappearance of 0.570×10^{-2} moles of 'S'. First order rate constants

TABLE I

'S' IN METHANOL—REACTION TEMPERATURE = 0° C.

Time, hr.	'S' reacted, moles × 10^{-2}	Total Cl^- produced, moles × 10^{-2}	H^+ produced, moles × 10^{-2}	Cl^- formed by dimerization, moles × 10^{-2}
(a) Initial 'S' concentration = 0.570 mole/liter at −78° C.				
14		0.090	Negligible	0.090
24	0.120	0.120	Negligible	0.120
48		0.254	Negligible	0.254
51	0.200		0.001	
98		0.304		
131	0.380		0.006	
194		0.431		
(b) Initial 'S' concentration = 1.140 moles/liter at −78° C.				
12	0.072	0.063	0.002	0.061
17	0.089	0.096	0.003	0.093
29.5	0.150	0.151	0.003	0.148
48	0.236	0.226	0.003	0.223
112	0.406	0.390	0.005	0.385

TABLE II

'S' IN METHANOL—REACTION TEMPERATURE = 25° C.

INITIAL 'S' CONCENTRATION = 1.140 MOLES/LITER AT −78° C.

Time, hr.	'S' reacted, moles × 10^{-2}	Total Cl^- produced, moles × 10^{-2}	H^+ produced, moles × 10^{-2}	Cl^- formed by dimerization, moles × 10^{-2}
0.5	—	0.062	—	—
1	0.088	0.089	0.004	0.085
2	0.193	0.200	0.006	0.194
3	0.287	0.264	0.008	0.256
4	0.341	0.317	0.009	0.308
8	0.447	0.471	0.013	0.458
12	0.480	0.482	0.016	0.466
19	—	0.509	—	—

TABLE III

'S' IN METHANOL—REACTION TEMPERATURE = 41.5° C.

INITIAL 'S' CONCENTRATION = 1.140 MOLES/LITER AT −78° C.

Time, hr.	'S' reacted, moles × 10^{-2}	Total Cl^- produced, moles × 10^{-2}	H^+ produced, moles × 10^{-2}	Cl^- formed by dimerization, moles × 10^{-2}
0.5	0.239	0.278	0.014	0.264
1	0.371	0.335	0.017	0.318
2	0.455	0.456	0.021	0.435
3	0.468	0.488	0.026	0.462
4	0.501	0.512	0.029	0.483
8	0.521	0.540	0.037	0.503
12	0.526	0.542	0.039	0.503

calculated on the basis of Cl^- formed by dimerization were not consistent throughout a run. A summary of initial rate constants is given in Table IV.

TABLE IV

SUMMARY OF FIRST ORDER INITIAL RATE CONSTANTS AND DATA FOR ARRHENIUS LINE

Temp., °A	$1/T \times 10^{-3}$	1.140 *M* 'S' solution		0.570 *M* 'S' solution	
		k initial, hr.$^{-1}$	$\log_{10}k$	k initial, hr.$^{-1}$	$\log_{10}k$
314.5	3.19	1.15	0.17	1.08	0.03
298.0	3.36	2.20×10^{-1}	$\bar{1}.30$	2.24×10^{-1}	$\bar{1}.35$
273.0	3.67	9.0×10^{-3}	$\bar{3}.95$	7.38×10^{-3}	$\bar{3}.87$

A linear relation is found by plotting $\log_{10}k$ against $1/T$ with the result that, for the dimerization of methyl-bis-β-chloroethylamine in methanol, k (initial) $= 4.0 \times 10^{13}e^{-19600/RT}$ hr.$^{-1}$.

Discussion

Validity of the Analytical Methods

Doubt exists as to the validity of gravimetric determinations of chloride ion with slightly acidified silver nitrate in 'S' or 'S'–HCl solutions. Marion's results (7) indicate that chloride ion production occurs quite readily at 100° C. in the dilute acid solution. It was shown by chloride analyses that 'S' is reasonably well stabilized by the addition of 50 ml. of 4 *N* nitric acid to a 10 ml. sample of a 0.550 molar solution of 'S' in methanol, and that determinations with silver nitrate by the previously described procedure, may be made in 'S' and/or 'S'–HCl solutions, the accuracy being about 1.5 mgm. of silver chloride. Thus, the maximum error arising from the analytical method used for chloride determination would be 2% and the method therefore is suitable for following the rate of chloride ion production in this investigation.

Subsequent investigations on the reactions of 'S' in nitric acid solution showed that there was probably some chloride ion produced, owing to hydrolysis in the course of heating. Fortunately this is counterbalanced by the solubility effect of nitric acid on silver chloride.

Improved analytical methods were developed after this phase of the investigation was completed and are discussed in the next paper of the series.

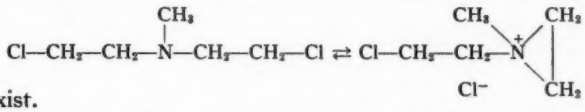
Reactions of 'S' in Methanol Solution

From the data in Tables I to III it appears that the production of chloride ion is practically the only process occurring at the temperatures indicated. A reaction producing hydrogen ion is present, but is not prominent. Furthermore, it is apparent that doubling the initial concentration of 'S' does not appreciably affect the rate, for given initial amount of 'S', at which chloride ion is produced. Thus it would appear that the initial reaction of 'S' in absolute methanol is one involving the unimolecular formation of chloride ion.

From the work of Marion (7) it appears that the principal product formed in a methanol solution of 'S' is its piperazinium dimer, which possesses two ionizable chlorines. It is concluded, therefore, that the formation of dimer, which should be a bimolecular reaction, is dependent upon a unimolecular process. Dimer formation, then, is not a result of direct reaction between two molecules of 'S' but is the result of a reaction involving an intermediate.

Hanby, Hartley, Powell, and Rydon (5) are in general agreement with these conclusions. They concluded that iminization is the rate-controlling process in the reaction of 'S' with water, and that dimer is the principal product formed when high concentrations of 'S' (11% by weight) are used.

It is known that β-bromoethylamine in aqueous solution is in tautomeric equilibrium with ethylenimine hydrobromide (1, 2, 3, 4, 6) and the presence of two β-chloroethyl groups in the 'S' molecule suggests that the equilibrium



might also exist.

However, first order rate constants were not consistent throughout a run, except in the reaction at 0° C. At the higher temperatures alcoholysis complicates the process by effecting a change in the medium. It is also possible that the true kinetics are obscured by the heterogeneity of the system.

The activation energy calculated from initial rates was found to be about 19.6 kcal. This is similar to that obtained for the ring formation reaction of other halogen alkyl amines. Most of the studies have been made by Freundlich and coworkers and are well reviewed by Salomon (10). In the light of this paper and the results obtained with subsequent work on the reaction of 'S' in acetone–water mixtures, the rate-controlling step of the mechanism is postulated to be polymolecular solvolysis of the chlorine atom assisted by the nucleophilic displacement ability of the nitrogen atom. The resultant intermediate ethylenimonium ion reacts very rapidly with 'S' or with one of its kind to form the dimer.

The production of hydrogen ion indicates the presence of a hydrolytic process in addition to dimerization. Since some hydrogen ion is formed and since 'S' is a weak base, it is logical that the small amount of hydrogen ion formed should immediately combine with 'S' (but would be analytically determined by the procedure used). Thus, at the point where the rate of 'S' disappearance falls off it might be that the 'S' remaining in the solution is stabilized by the formation of the hydrochloride.

The equilibrium

$$CH_3OH + CH_3OH \leftrightarrows CH_3OH_2^+ + CH_3O^-$$

is known to exist in methanol. Broensted has called methanol an "Amphiprotic" solvent since it is able to receive or lose a proton. Conversely, it is able to give or lose an electron. Its ability to convert a covalent bound chlorine atom to the ionic state may be due to this property. In the conversion process

of the 'S' molecule the intermediate ethylenimonium ion is momentarily stabilized by the presence of the active tertiary nitrogen. However, this represents a strained system, and polymeric transformation must occur for complete change. It is quite conceivable that before this action can occur a methylate of 'S' may be formed.

The results of this investigation may be compared with those of Mason and Block (8), who investigated the polymerization of β-4-morpholinoethyl chloride and found that 34% of the compound was converted to N,N¹-β-dispiromorpholinepiperazinium dichloride when an ethanol solution containing 5 gm. of the compound was refluxed for 24 hr. Evaporation of the alcohol after removal of the solid piperazinium dichloride gave them a solid which they identified as β-4-morpholinoethyl ether.

Since 'S' contains a second β-chloroethyl group it is to be expected that the dimerization of 'S' would proceed much more quickly than the dimerization of β-4-morpholinoethyl chloride.

References

1. FREUNDLICH, H. and NEUMANN, W.Z. Phys. Chem. 87 : 69. 1914.
2. GABRIEL, S. Ber. 21 : 566. 1888.
3. GABRIEL, S. Ber. 21 : 1049. 1888.
4. GABRIEL, S. Ber. 21 : 2664. 1888.
5. HANBY, W. E., HARTLEY, G. S., POWELL, E. O., and RYDON, H. N. J. Chem. Soc. 519. 1947.
6. HOWARD, C. C. and MARCKWALD, W. Ber. 32 : 2036. 1899.
7. MARION, L. Private communication.
8. MASON, J. P. and BLOCK, H. W. J. Am. Chem. Soc. 62 : 1443. 1940.
9. OGSTON, A. G. Private communication.
10. SALOMON, G. Trans. Faraday Soc. 32 : 153. 1936.
11. THOMPSON, A. L., HARDWICK, T. J., HAY, A. W., and WINKLER, C. A. Can. J. Research, B, 26 : 161. 1948.

The authors wish to acknowledge the assistance of the Defence Research Board in procuring the information referred to as 'private communications'.

KINETIC STUDIES ON METHYL-BIS-β-CHLOROETHYLAMINE

IV. THE KINETICS OF DIMERIZATION IN AQUEOUS ACETONE[1]

A. L. THOMPSON,[2] T. J. HARDWICK,[3] AND C. A. WINKLER

Abstract

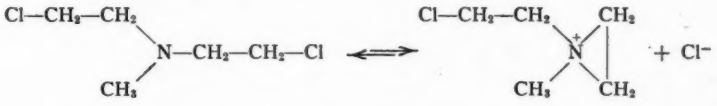
The kinetics of the reactions of methyl-bis-β-chloroethylamine in acetone–water solutions which were 2, 4, 8, 16 and 27 *M* with respect to water have been studied. The principal reaction forms a piperazinium dimer, but hydrolysis also occurs. The rate has been found essentially first order with respect to disappearance of the amine in solutions 27 *M* in water. In solvents of lower water content the first order rate constants are unsatisfactory owing to changes in water content of the medium and retardation by chloride ion.

Introduction

Characteristic of methyl-bis-β-chloroethylamine ('S') is its reactivity in the presence of water. One opinion is that hydrolysis is the main reaction of free 'S' in water, while a second opinion holds dimerization to be the main course followed.

Cohen (2) found the rate of chloride ion formation in the reaction between 'S' and water to be approximately first order. He postulated intermediate formation of an imine ring which reacted either with itself or with 'S' to form dimer.

The postulate of imine formation of 'S' may be similar to the case of β-bromoethylamine, which has been shown to exist in tautomeric equilibrium with ethyleneimine hydrobromide (1, 5, 7). With 'S' the presence of two β-chloroethyl groups suggests the possibility that equilibrium between 'S' and the corresponding imine might exist.



Recent work by Jones and coworkers (6) on the reactions of ethyleneimine itself shows that the quaternary nitrogen hydrochloride $H_2N—CH_2—CH_2—Cl$ .HCl is quite unstable and reverts slowly to ethyleneimine. The decomposition is markedly increased by solution in water where the cyclic compound is the more stable. With 'S' the presence of the other groups stabilizes the nitrogen, but the effect of water in causing iminization probably still persists.

[1] *Manuscript received in original form February 17, 1947, and, as revised, November 17, 1947.*

Contribution from the Physical Chemical Laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council.

[2] *Holder of a Studentship under the National Research Council of Canada. Present address: Radiation Laboratory, McGill University.*

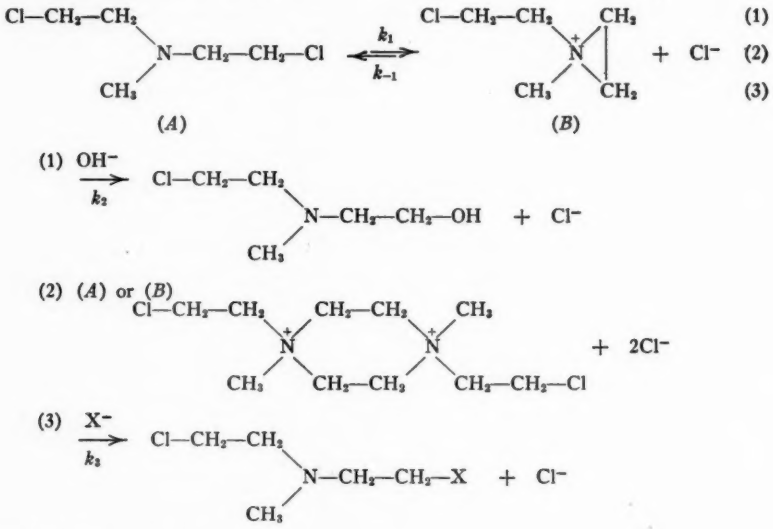
[3] *Holder of a Studentship under the National Research Council of Canada. Present address: National Research Council, Chalk River Laboratory, Chalk River, Ont.*

In a review of the work of Freundlich and coworkers, Salomon (8) has discussed the tendency towards iminization of a series of chlorinated primary amines. The general reaction studied was:

$$Br{-}CH_2{-}(CH_2)_n{-}NH_2 \longrightarrow [CH_2{-}CH_2{-}\cdots{-}NH_2]^+ + Br^-$$

The imine formation was found to be strictly first order and generally independent of pH. In anhydrous organic solvents the reaction proceeded slowly; in water, rapidly; and in solvent mixtures the rate varied with the water concentration. With different chain-lengths the ease of iminization is altered, the rate of cyclization decreasing with the number of atoms in the chain in the order 5, 6, 4, 3.

Bartlett and coworkers (1) have investigated the reaction of 'S' in 67% acetone, 33% water at 23° C., and have presented a useful scheme for the mechanism of the reactions of 'S' that may take place, through the intermediate step of imine formation.



where (1) is hydrolysis,

(2) is the dimerization process,

(3) is the competition reaction by another ion e.g. $S_2O_3^=$.

They are of the opinion that the reactivity of 'S' in water is due to the relative ease of iminization. Which of the three subsequent reactions takes place depends on the relative concentrations of OH^-, (*A*) or (*B*), and X^- in aqueous solution. In their work they found that dimer was the principal product of the reaction.

In an attempt to determine the influence of water on the dimerization of 'S', a detailed study of the reaction has been made using 'S' in acetone solution

containing 2, 4, 8, 16, and 27 molar water. With solutions 16 and 27 *M* with respect to water, complete homogeneity existed throughout the course of the reaction, since all products were soluble.

Experimental

(*a*) *Materials and Method*

The 'S' obtained in the form of impure 'S'–HCl, was separated from its impurities by dissolving the solid in cold water and adding ammonium hydroxide until the solution was basic to litmus. Cold benzene was added and the 'S' extracted in the upper layer. The excess benzene was distilled off and the remaining concentrate of 'S' was vacuum distilled, the fraction distilling at 85° to 90° C. being collected at the pressure used. To prevent reaction of 'S' itself the purified product was stored in dry ice.

The acetone used in these experiments was Merck's Reagent Grade. The solutions containing 2, 4, and 8 *M* water were prepared by dissolving a weighed amount of 'S' in acetone at 0° C., adding the appropriate amount of water and diluting to a standard volume with acetone. The solution could not be prepared at lower temperatures because the water froze out from the acetone. However, analysis showed that no chloride ion was produced during this procedure. The solutions were stored in dry ice. Aliquot portions were heated in sealed Pyrex bulbs placed in thermostats.

The systems containing 16 *M* and 27 *M* water were homogeneous throughout the reaction; hence it was convenient to adopt a more rapid technique. At first the reaction was initiated by mixing the acetone solution of 'S' and the water in appropriate amounts which had previously been thermostatically controlled at the reaction temperature. However, it was found that this caused an initial temperature rise which could not be controlled by the thermostat. The technique finally adopted was to mix the water and acetone, bring the solution to the required temperature, and crush a bulb containing a weighed amount of 'S' in the solution. Samples were withdrawn by means of a pipette and drained into a known excess of standard dilute nitric acid.

(*b*) *Analytical Procedure*

The following procedure was adopted for the analysis of the reaction products of 'S' in water–acetone. It provides for the simultaneous analysis of unreacted 'S', chloride ion, and hydrogen ion in a sample of unreacted or partially reacted 'S'.

Distilled water (20 ml.) was placed in a 250 ml. electrolytic beaker. Standard dilute nitric acid was run into the water in excess of the amount required to neutralize the free 'S'. The sample to be analyzed was poured into this acid solution, the bulb being washed with distilled water and the solution diluted to 75 ml. The solution was cooled to 0° C. and titrated at that temperature with sodium hydroxide (0.2 *N*) to a pH 3.8. This corresponds to 'S' nitrate in solution. Thus the initial amount of nitric acid in excess of that neutralized by the sodium hydroxide is equivalent to the unreacted

'S' in solution. It may be considered as approximate that any hydrolyzed 'S' will be neutralized by the hydrogen ion produced in the hydrolysis. The solution was then brought to pH 5 to 6 and the chloride ion determined argentometrically using an Ag : AgCl electrode. The end point for this titration, using a calomel electrode as a reference electrode, was +270 millivolts. The alkali titration was continued rapidly to pH 8.5 (end point for $'S'H^+ \rightarrow 'S' + H^+$). In this case 'S' includes any hydrolysis products which will retain basicity similar to that of the original compound. Thus hydrogen ion production is given approximately by the difference in alkali titre between pH 3.8 and 8.5 and the value previously obtained as a measure of free 'S'. Although this method is only approximate, it serves the purpose intended; that is, to differentiate between a hydrolysis reaction and dimerization. It was shown experimentally that the determinations for unreacted 'S' and chloride ion are accurate to 1.5%.

Results

A portion of the results obtained in the investigation are presented in Tables I to VI. The reaction rate data for all temperatures are summarized in Table VII, where initial rates are recorded, since in all except one case (27 *M* water) calculated *k* values showed marked falling-off as reaction proceeded.

The pH values were measured directly with a glass electrode and calomel reference electrode. No attempt has been made to correct for changes in boundary potential.

When the results in Table I are compared with the rate data which are presented in Tables II (*b*) and III (*a*) there is found to be good agreement with the general relation that the reaction rate is greater for higher initial pH; also the rate is rapidly decreased with decrease in pH as the reaction progresses.

TABLE I

DATA ON THE pH OF THE REACTION SYSTEMS (2 *M* AND 4 *M* WATER)

Temperature, 25° C.

Reaction time, hr.	pH of 0.284 *M* 'S' soln. in acetone	
	2 *M* water	4 *M* water
0	6.0	7.4
23	6.0	6.1
80	5.8	5.6

It is observed that dimer formation from 'S' in a 1 : 1 mixture of acetone and water is essentially first order rate dependent. The disappearance of 'S' and chloride ion production differ by an amount equivalent to the hydrolysis that occurred simultaneously. The decrease in rate towards the end of the

TABLE II

REACTION OF 'S' IN ACETONE – 2 *M* WATER

Time, hr.	Milliequivalents of					
	'S' disappeared*		Cl^- formed		H^+ produced	
	(1)	(2)	(1)	(2)	(1)	(2)
(*a*) *Temperature = 41.0° C.* (1) Initial concentration of 'S' = 0.574 *M* (2) Initial concentration of 'S' = 0.284 *M*						
0.5	0.10	—	0.075	—	—	—
2	0.15	0.14	0.13	0.12	0.01	0.01
4	0.20	0.20	0.20	0.22	0.02	0.02
7	0.35	0.26	0.30	0.24	0.02	0.05
18	0.40	0.43	0.40	0.41	0.03	0.05
36	0.60	0.59	0.53	0.56	0.05	0.05
48	0.79	0.80	0.80	0.76	0.07	0.06
(*b*) *Temperature = 25° C.* Initial concentration of 'S' = 0.284 *M*						
4		0.18		0.12		0.01
10		0.20		0.18		0.02
19		0.25		0.22		0.03
44		0.44		0.43		0.04

* *In this and subsequent tables, "'S' disappeared" is the disappearance of the amine to produce dimer.*

The data in Column (1) of Table II, (a), were obtained with 5 ml., those in Column (2) with 10 ml., of stock solution. Thus the results are directly comparable.

TABLE III

REACTION OF 'S' IN ACETONE – 4 *M* WATER

Initial concentration of 'S' = 0.284 *M*

Time, hr.	Milliequivalents of		
	'S' disappeared	Cl^- formed	H^+ produced
(*a*) *Temperature = 25° C.*			
2	0.13	0.14	Negligible
5	0.25	0.27	Negligible
12	0.44	0.46	0.01
24	0.75	0.82	0.02
48	1.05	1.12	0.02
168	2.00	2.02	0.03
(*b*) *Temperature = 100° C.*			
0.5	0.70	0.62	0.05
1	0.90	0.95	0.15
2	1.10	1.34	0.21
5	1.38	1.74	0.40
8	1.65	2.08	0.50
21	—	—	0.99
55	—	2.76	—

TABLE IV

REACTION OF 'S' IN ACETONE – 8 *M* WATER

Initial concentration of 'S' = 0.100 *M*

Temperature = 25° C.

Time, hr.	Milliequivalents of		
	'S' disappeared	Cl^- formed	H^+ produced
2	0.160	0.144	Negligible
4	0.200	0.170	Negligible
8	0.260	0.276	0.005
16	0.310	0.310	0.01

TABLE V

REACTION OF 'S' IN ACETONE – 16 *M* WATER

Initial concentration of 'S' = 0.100 *M*

Temperature = 24.7° C.

Time, min.	Milliequivalents of			k, $min.^{-1}$
	'S' disappeared	Cl^- formed	H^+ produced	
4.00	—	0.077	Negligible	1.97×10^{-2}
8.25	0.135	0.138	"	1.79
14.5	0.215	0.218	"	1.70
25.5	0.310	0.317	"	1.49
38.5	0.380	0.385	"	1.40
57.0	0.460	0.469	"	1.11
77.7	0.535	0.546	0.01	1.01
97.7	0.590	0.606	0.03	0.951
119	0.620	0.645	0.04	0.870
157	0.680	0.716	0.045	0.800
1160	—	0.976	—	—

reaction appears to be due mainly to a decrease in pH (Fig. 1). At this stage of the reaction some of the unreacted 'S' is in the less reactive form $'SH^+$. Bartlett (1) claims to have found inhibition by sodium chloride in the system which he studied. The addition of sodium sulphate showed no change in rate, however, indicating the absence of neutral salt effects. The rate of quaternary chloride formation for a 1 : 1 acetone water system is expressed quite accurately by:

$$k = 5.2 \times 10^{11}\, e^{-17900/RT}\ min.^{-1}$$

The series of experiments on the reaction of 'S' in acetone–water may be conveniently divided into two classes: (*a*) those in which dimer was precipitated, and (*b*) those where homogeneous conditions prevailed throughout the

TABLE VI*

REACTION OF 'S' IN ACETONE – 27 *M* WATER

Initial concentration of 'S' = 0.100 *M*

Temperature = 24.7° C.

Time, min.	Milliequivalents of				k, min^{-1}
	'S' disappeared	Cl^- formed		H^+ produced	
		(1)	(2)		
1.85	0.090	0.084	0.080	Negligible	4.77×10^{-2}
3.90	0.180	0.176	0.180	"	4.96
5.85	0.250	0.243	0.235	"	4.78
8.00	0.305	0.310	0.310	"	4.79
9.85	0.370	0.380	0.375	"	4.85
12.25	0.435	0.444	0.440	"	4.79
14.0	0.480	0.486	0.490	"	4.77
17.2	0.540	0.552	0.550	"	4.64
24.8	0.650	0.662	0.670	"	4.37
30.0	0.700	0.713	0.710	0.005	4.16
35.3	0.720	0.730	0.740	0.01	3.68
43.1	0.730	0.756	0.745	0.03	3.27
60	0.780	0.820	0.810	0.05	2.88

** In Table VI, the data in the second column (2) of "Cl^- formed" are values read from the experimental curve for the reaction of 0.075 M 'S' and recalculated to a 0.100 M basis.*

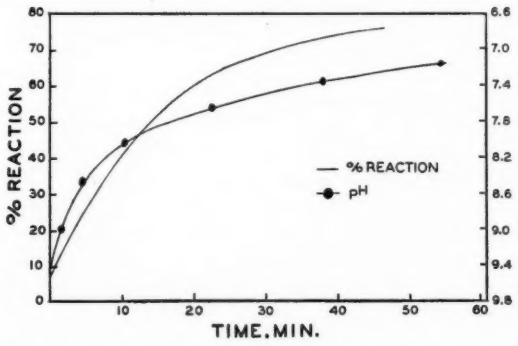


FIG. 1. *Change in pH as reaction progresses at 25° C. in a 0.100M solution of 'S' in acetone–water mixture (50–50) (volume ratio).*

course of the reaction. The first group consists of experiments in which the water concentration was 2, 4, and 8 molar, and is reported in Tables II to IV. The second class includes the dimerization reaction which takes place in 16 and 27 *M* water, the results of which are to be found in Tables V and VI. Several generalities which exist throughout all systems studied are as follows:

TABLE VII

SUMMARY OF DATA FOR CALCULATION OF ACTIVATION ENERGIES FROM INITIAL RATES OF 'S' DIMER FORMATION IN ACETONE–WATER MIXTURES

Temp., °A	$1/T \times 10^{-3}$	k, min.$^{-1}$	$\log_{10} k$
(*a*) *4 M water*			
298	3.36	1.07×10^{-4}	$\bar{4}.03$
314	3.18	3.50×10^{-4}	$\bar{4}.54$
345	2.90	1.02×10^{-3}	$\bar{3}.01$
373	2.68	2.90×10^{-2}	$\bar{2}.46$
(*b*) *8 M water*			
298	3.36	9.3×10^{-4}	$\bar{4}.97$
311	3.22	2.9×10^{-3}	$\bar{3}.46$
332	3.01	9.3×10^{-3}	$\bar{3}.97$
345	2.90	1.66×10^{-2}	$\bar{2}.22$
(*c*) *16 M water*			
273.1	3.36	1.60×10^{-3}	$\bar{3}.20$
282.3	3.54	4.10×10^{-3}	$\bar{3}.61$
297.8	3.36	1.95×10^{-2}	$\bar{2}.29$
(*d*) *27 M water*			
273.1	3.66	2.80×10^{-3}	$\bar{3}.45$
282.3	3.54	8.80×10^{-3}	$\bar{3}.95$
297.8	3.36	4.80×10^{-2}	$\bar{2}.68$

(1) The rate of reaction is dependent upon the nature of the solvent used, specifically its water content. The actual relation of the k values to the amount of water cannot be formulated simply, but the increase in rate becomes disproportionate at higher water concentrations (i.e., those experiments made with solutions which were homogeneous throughout the reaction). In those solutions where dimer was precipitated the decrease in the measured rate may be due to the removal of water from the solution by the dimer.

(2) The rate of reaction of 'S' in acetone–water is independent of the initial amine concentration (see Tables II and VI). Although experiments to verify this have been made only with 2 M and 27 M water, it is not unreasonable to assume that in the intermediate water concentrations the rate of the reaction will likewise be independent of 'S' concentration.

(3) Although the results are not suitable for mathematical analysis, certain reasons for the changing rate constants are indicated. When a considerable production of hydrogen ion occurs a rapid decrease in the first order k values is noticed (Table III). This is probably due to the reaction of 'S' with the

hydrogen ion produced to form 'S'H$^+$ which cannot undergo iminization. Thus the concentration of free 'S' in solution is considerably reduced. Strong inhibition of the reaction is apparent after the initial stages of the reaction. This may be due to the salt effects caused by the dimer ion, although no further retardation was observed by the addition of 0.15 *M* sodium sulphate. Chloride ion inhibition may be the major cause of the decrease in rate, since Bartlett (1) found a diminished rate when sodium chloride was added.

(4) The difference between chloride ion production and 'S' disappearance corresponds in nearly all cases to the formation of hydrogen ion. The degree of hydrolysis does not seem to be greatly influenced by the water concentration, but is quite dependent on temperature. As will be seen by comparison with the results published in a subsequent paper (4), the temperature required to effect appreciable hydrolysis of free 'S' is of the same order as that required to hydrolyze the chlorines on the 'S'H$^+$ ion. This indicates that hydrogen ion is produced by an identical reaction, which is postulated as the direct replacement of β-chlorine by hydrolysis. The relatively small production of hydrogen ion, especially at low temperatures, serves as further evidence that the intermediate imine is reasonably stable to water.

Linear relations are found by plotting $\log_{10} k$ against $1/T$ for all water concentrations except 2 *M*. An unusual feature arising from these results is that as the water content of the solvent increases, both the rate and the activation energy increase (Table VIII).

TABLE VIII

VALUES FOR THE PARAMETERS OF THE ARRHENIUS EQUATION $K = Be^{-E/RT}$ FOR THE REACTION OF 'S' IN VARIOUS MIXTURES OF ACETONE AND WATER

Water concentration*	$k_{relative}$ at 25° C.	*E*, kcal.	$\log_{10} B$
4 *M*	1	10	3.3
8 *M*	10	12	5.8
16 *M*	200	17.4	11.05
27 *M*	480	17.9	11.73

* *The values in this column merely indicate changes in solvent composition and are not used in the calculation of any reaction rate constant.*

Discussion

The kinetics of the reaction of 'S' in water itself are complex and in acetone-water mixtures, at lower water concentrations, are further complicated by changes in medium. In the systems studied the process is essentially first order in solvent of given water content, with the formation of the ethyleneimonium ion postulated as the rate-governing step. This ion presumably reacts very rapidly with itself or with 'S' to form dimer. The intermediate is formed by

the action of water in the reaction medium on the chlorine atom and by the nucleophilic displacement powers of the nitrogen nucleus.

Bartlett (1) has investigated the effect of pH on the reactions of a series of β-chloroethylamines. In decreasing order of basic strength, those studied were diethyl-β-chloroethylamine, methyl-bis-β-chloroethylamine ('S'), and bis-β-chloroethylamine. The first undergoes dimerization following quite exactly a first order rate with negligible hydrolysis. With the second, dimerization is the principal reaction in water, but the rate is markedly influenced by changes in medium. The first order rate is not as uniform as with the first compound. The principal reaction of the third amine is hydrolysis, although some dimerization has been observed. From these results he concluded that the greater the basicity of the nitrogen nucleus, whether this basicity is due to the surrounding medium, or inherent in the compound itself, the greater is the temporary stabilization of the intermediate. Bartlett, however, assumes that hydrolysis occurs by splitting of the imine ring by water or hydroxyl ion. He does not include the possibility that hydrolysis of the chlorine atoms may occur directly, i.e., not involving the nitrogen nucleus. Dimerization is considered to occur if the stabilization period is long enough to allow favorable collision previous to the intervention of hydrolysis.

A rather surprising result obtained from these investigations on 'S' is the fact that as the water content of the solvent is increased, the activation energy as well as the rate of dimerization increases (Table VIII). Salomon (8) has observed a somewhat similar phenomenon in the reaction:

$$Cl—(CH_2)_5—NH_2 \rightleftharpoons (CH_2)_5{=}NH \cdot HCl$$

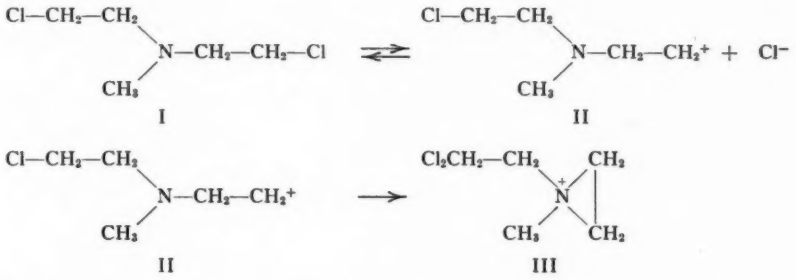
Cox (3) has obtained results of a similar nature for the reaction of bromoacetophenone with aniline in a variety of solvents.

Salomon explains this simultaneous increase of k and E with increasing water concentration as due to a water sheath which is formed about the nitrogen atom. The effect of this surrounding water layer is to inhibit the ring closure process. He assumes that conditions which produce a large probability factor are unfavorable in solvents containing lower concentrations of water, consequently the rate is considerably reduced.

Wynne-Jones (9) has made the suggestion that in such reactions there may be a slight change in the mechanism, as the activated complex may be affected to a certain extent from one system to another.

The suggestion of Salomon (8) has been modified to explain the relative changes in k and E observed here. The dimerization of 'S' differs from the systems which he studied in that a subsequent bimolecular process is necessary to ensure stability, but the stability of the imine seems great enough to consider its formation a definite and decisive step in the mechanism, with subsequent changes of little import as long as they have no effect on the rate of the reaction, or influence the course of the primary change.

The formation of the ethyleneimonium ion may be considered to take place in two steps:



The reaction I → II is considered to be in equilibrium. The concentration of II relative to I will depend upon the solvolytic power of the medium on the β-chlorine atoms, and upon the temperature. With higher concentrations of water, the solvolytic ability of the water–acetone should increase, causing a larger number of 'S' molecules to proceed to the form II. The reaction of II to produce III is postulated as the rate-governing step. With increasing water concentration the water sheath surrounding the nitrogen nucleus will increase in size and take a more prominent part in the tendency of the $N—CH_2—CH_2$ towards ring closure. The presence of the water layer necessitates a higher activation energy to permit ring closure.

Thus an increase of water increases the concentration of the intermediate II. Although the activation energy of ring closure is increased, resulting in a decrease of the exponential $e^{-E/RT}$, the fraction of molecules in condition to be activated has increased considerably. Therefore, there will be a net increase in the total number of molecules II in the activated state, which manifests itself as an increase in the measured rate.

The solvolytic effect is due mainly to the amount of water present. Any influence which will cause the amount of water to decrease, such as salt effects, is likely to decrease the rate. This is borne out by a comparison of the results obtained for the dimerization of 'S' in 2 *M* and 27 *M* water. With 2 *M* water the *k* values rapidly decrease as reaction progresses. The dimer precipitated as a fluffy mass as soon as it formed. This crystal form undoubtedly tends to remove water from the solution, which results in a decrease of the actual water available for maintaining the solvolytic strength of the solution. With 27 *M* water, however, no precipitate is formed and the *k* values are reasonably constant throughout the experiment.

Question might be raised concerning the stability of the molecule II. It is to be noted that hydrolysis is negligible at temperatures below 72° C. even when the water concentration is 27 *M*. A comparison with the results in (4) shows that hydrolysis below 70° C. does not occur during the time of reaction of 'S' in acetone–water. It is believed that hydrolysis of $'S'H^+$ occurs through direct attack on the β-chlorine and not through reaction with the imine inter-

mediate. The source of hydrolysis products in this case must be reaction of hydroxyl ion and the intermediate II. Certainly the production of hydrogen ion comes from a process having a higher activation energy. The activation energy for hydrolysis of β-chlorine atoms in acid solution is 23 to 25 kcal. and will likely be higher in the less polar acetone–water medium.

Bartlett (1) found the rate of dimerization of 'S' in pure water to be inhibited by the presence of sodium chloride. The effect of chloride ion would be to shift the equilibrium I $\rightarrow$ II to form free 'S'.

References

1. BARTLETT, P. D. Private communication.
2. COHEN, B. Private communication.
3. COX, H. E. J. Chem. Soc. 119 : 142. 1921.
4. HARDWICK, T. J., THOMPSON, A. L., and WINKLER, C. A. Can. J. Research, B, 26 : 193. 1948.
5. HANBY, W. E., HARTLEY, G. S., POWELL, E. O., and RYDON, H. N. J. Chem. Soc. 519. 1947.
6. JONES, G. D., LANGSJOEN, A., NEUMANN, SISTER M. M. C., and ZOMLEFER, J. J. Org. Chem. 9 : 125. 1944.
7. OGSTON, A. G. Private communication.
8. SALOMON, G. Trans. Faraday Soc. 32 : 153. 1936.
9. WYNNE-JONES, W. F. K. Trans. Faraday Soc. 32 : 175. 1936.

The authors wish to acknowledge the assistance of the Defence Research Board in procuring the information referred to as 'Private communication'.

KINETIC STUDIES ON METHYL-BIS-β-CHLOROETHYLAMINE

V. THE REACTIONS IN VARIOUS ACID SOLUTIONS[1]

T. J. HARDWICK,[2] A. L. THOMPSON,[3] AND C. A. WINKLER

Abstract

The hydrolysis of the quaternary ammonium salts of methyl-bis-β-chloroethylamine is inhibited by both hydrogen ions and chloride ions. The kinetics of hydrolysis in various anion solutions suggest that reaction occurs by direct attack at the β-chlorine atoms by hydroxyl ion.

Introduction

The stability of methyl-bis-β-chloroethylamine hydrochloride, 'S'–HCl, has been discussed by Marion (3) and others (2,6). Since these investigators fail to agree, a detailed investigation of the reaction of methyl-bis-β-chloroethylamine in aqueous solution was made in an effort to determine the stability of the hydrochloride. This reaction may be expressed generally by the following equation:

$$RCl_2 + 2HOH \longrightarrow R(OH)_2 + 2Cl^- + 2H^+$$

It soon became apparent that the anion might play an important part in the reaction rate and course. Accordingly the study was extended to include the reactions of 'S'H^+ ion in dilute acid in the presence of various anions.

Experimental

(a) *Materials and Method*

'S' was weighed directly into a dilute solution of acid, in excess of the amount required to neutralize the amine. The sample was shaken until all the 'S' had reacted with the acid to form the 'S'H^+ ion. Formation of chloride ion was not detectable during the preparation. The solution was diluted with freshly distilled water to a standard volume, from which aliquot portions (10 ml.) were sealed into Pyrex bulbs and placed in thermostats. Blank analyses were made on all solutions.

(b) *Analytical Procedure*

1. Determination of H^+ and Cl^- Formation

The sample was diluted to approximately 50 ml. and titrated with sodium hydroxide (0.1 *N*) to pH 3.8 (the end point for the reaction 'S' + $H^+ \rightarrow$ 'S'H^+). This titre measures the total hydrogen ion in solution. Subtraction of the amount of hydrogen ion present in the blank analysis determines the hydrogen ion produced by hydrolysis.

[1] *Manuscript received in original form February 17, 1947, and, as revised, November 17, 1947. Contribution from the Physical Chemical Laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council of Canada, Ottawa, Ont.*

[2] *Holder of a studentship under the National Research Council of Canada. Present address: National Research Council, Chalk River Laboratory, Chalk River, Ont.*

[3] *Holder of a studentship under the National Research Council of Canada. Present address: Radiation Laboratory, McGill University, Montreal.*

The solution was brought to pH 6, where chloride ion was determined argentometrically using an Ag:AgCl electrode.

2. *Determination of Nitrate Ion*

In the reaction of 'S'H^+ in nitric acid, results were such that the determination of nitrate ion was advisable. Chloride ion, which seriously interferes with the analysis, was first removed by argentometric precipitation. The subsequent procedure was that given by Scott (7).

3. *Systems Studied*

The reactions of 'S'H^+ over a suitable range of temperatures (72°, 100°, 116°, 130° C.) have been studied in the following acid solutions: slight excesses of (1) hydrochloric, (2) nitric, (3) sulphuric, and (4) same as (1) but with added sodium sulphate; also a greater excess of (5) sulphuric, (6) nitric and (7) benzenesulphonic acids. Typical data at the reaction temperature of 72° C. are presented in Tables I and II. Further studies were made of 'S' in benzenesulphonic acid solution over a wide range of relative concentrations and with added sodium chloride.

Results

In general, inhibition of hydrolysis occurs as the reaction progresses. This decrease in rate is most likely due to a decrease in hydroxyl ion concentration, caused by the formation of hydrogen ion as a hydrolysis product, and by chloride ion, which has been shown to exhibit a retarding effect. To allow for the change in medium, a correction factor has been applied to the usual first order rate expression. An empirical equation of the form

$$k = \frac{2.3}{t} 10^{10x} \log \frac{a}{a - x}$$

gives good agreement with the experimental data except with benzenesulphonic acid, where a correction factor of 10^{5x} is more appropriate. In the modified equation, a is $2[\text{'S'H}^+]_0$ and x is H^+ produced by hydrolysis in time t.

As in reactions with dimer (8), the two β-chlorine atoms are assumed to be hydrolyzed independently, hence the apparent concentration of β-chlorine atoms is double the 'S'H^+ concentration. This equation accounts reasonably well for the rate of hydrolysis of 'S'H^+ in slight excesses of hydrochloric and nitric acids, and a greater excess of sulphuric. Secondary reactions are observed where hydrolysis takes place in nitric acid medium.

Owing to changes of pH with temperature, the calculation of the activation energy must be considered only approximate. In calculation of the data for the Arrhenius lines, initial rates were used throughout.

From the data presented in Table I it is evident that 'S'H^+ in the presence of a slight excess of hydrochloric acid suffers displacement of the β-chlorine atoms through hydrolysis only. The observed k values agree reasonably well. It is obvious from the rate equation ($k = 3.1 \times 10^{-12}\, e^{-22000/RT}$) that

aqueous solutions of 'S'–HCl will be stable at ordinary temperatures for a long time. The value for k at 25° C. is approximately 2.7 yr.$^{-1}$. The value of $t_{1/2}$ is readily calculable:

$$t_{1/2} = \frac{2.3}{k} 10^{10a} \log 2$$

$$= 3 \text{ years for } 0.1\ M \text{ solution 'S'–HCl with a slight excess of hydrochloric acid initially.}$$

This equation indicates that stability increases rapidly with increase in initial concentration. For systems where the initial pH is higher than that of the system studied here it should be possible to interpolate approximately by

TABLE I

REACTION OF 'S'H$^+$ IN DILUTE SOLUTIONS OF (1) HYDROCHLORIC ACID, (2) NITRIC ACID, (3) SULPHURIC ACID, (4) HYDROCHLORIC ACID + 0.200 M SODIUM SULPHATE

Initial concentration of 'S'H$^+$ = 0.0840 M
Excess H$^+$ over that required to neutralize 'S' = 0.0300 N
H$^+$ and Cl$^-$ required for complete reaction = 1.68 me.
Reaction temperature = 72° C.

	Time, hr.	Milliequivalents of		k, hr.$^{-1}$
		H$^+$ produced	Cl$^-$ produced	
(1)	3	0.080	0.110	—
	11	0.200	0.206	3.9×10^{-2}
	22	0.312	0.315	4.2
	32.5	0.390	0.380	4.5
(2)	1	0.083	0.110	—
	2	0.153	0.174	6.66×10^{-2}
	6	0.260	0.333	4.95
	14	0.412	0.459	4.78
	24	0.508	0.572	4.83
	36	0.618	0.715	5.3
	70	0.676	0.840	—
(3)	0.5	0.078	0.204	—
	1	0.167	0.300	—
	2	0.259	0.408	—
	4	0.310	0.468	—
	9	0.466	0.644	—
	21	0.582	0.800	—
	48	0.756	0.900	—
(4)	2	0.332	0.508	—
	4	0.428	0.680	—
	9	0.560	0.828	—
	23	0.669	0.972	—

The rate equation was not applicable to Systems 3 and 4 since several reactions proceeded concurrently as will be shown later.

introduction of the proper factor (i.e., change in hydrogen ion concentration) in the correction term.

The rate of hydrolysis is greater in nitric acid excess than in hydrochloric acid of the same excess. This may be due to a slight difference of pH, but is more likely due to inhibition by chloride ion. The values of k for nitric acid

solutions are not as regular as those for the reaction in hydrochloric acid, and a secondary reaction which is quite prominent at the higher temperatures causes the disappearance of hydrogen ion. Analyses for nitrate ion show that it disappears at approximately the same rate as hydrogen ion. This may indicate that the nitric acid breaks up into water and oxides of nitrogen, thus removing H^+ and NO_3^- from the system, or that an esterification reaction between the nitric acid and 'S'H^+-diol occurs, with an activation energy higher than that for hydrolysis of the chlorine atoms from 'S'H^+. The former postulate is the more probable.

In discussing the reactions of 'S'H^+ in dilute sulphuric acid and in dilute hydrochloric containing sodium sulphate, the acid–base equilibrium which exists in acid solutions of 'S' must be considered.

$$\text{'S'}H^+ \rightleftharpoons \text{'S'} + H^+$$

In dilute sulphuric acid solutions the ionization of the secondary hydrogen is insufficient to neutralize completely the 'S' present, consequently reactions characteristic of free 'S' in water should be observed. This is manifested in the increase of chloride ion production over that of hydrogen ion. Since dimerization results in the production of chloride ion from 'S' (8) mole for mole, without formation of hydrogen ion, this process is postulated as the reason for the discrepancy between H^+ and Cl^- production. After a certain fraction of the 'S'H^+ has been hydrolyzed there is sufficient hydrogen ion produced to neutralize the remaining free 'S' and subsequent action will be almost entirely one of hydrolysis of the 'S'H^+ ion.

The reaction of 'S'–HCl containing 0.2 *M* sodium sulphate is another example of a similar type of reaction. The sulphate ion removes hydrogen ion from solution and from 'S'H^+ to form HSO_4^-. Since the system then contains free 'S' and 'S'H^+ ion, its reactions will be similar to those of 'S'H^+ ion in dilute sulphuric acid.

In 'S'–HCl system with added sodium sulphate it was noticed (Table I (4)) that although chloride ion production was in excess of hydrogen ion production, the rate of reaction of 'S'H^+ with sodium sulphate present was considerably greater than in the absence of the sulphate. This difference is believed due to the relative hydroxyl ion concentration of the solutions. In the reaction of 'S' in dilute hydrochloric acid, the pH of the initial solution was 2, a value which gradually decreased to about 1 as the reaction progressed. On the other hand where sodium sulphate was present, the pH was greater than 3.8 and remained so until the free 'S' had been removed from solution by dimerization or by neutralization to form 'S'H^+. The ratio of concentrations of hydroxyl ion in the former case to that where free 'S' is present is about 200 : 1. From these results it appears that hydroxyl ion concentration has an appreciable effect on the rate and is probably a factor in the rate controlling process for the hydrolysis.

Studies made in acid solutions of higher concentrations confirm qualitatively the influence of pH on the reaction and permit examination of the effect of the

anion. The close agreement between hydrogen ion and chloride ion production indicates that no dimerization occurred during the hydrolysis of 'S'H$^+$ in the presence of a large excess of sulphuric acid, where there is ample hydrogen ion from the primary dissociation of the acid to maintain the amine in the quaternary form.

With large initial excess of nitric acid the rate was decreased by one-third as compared with that in dilute nitric acid where the excess was five times

TABLE II

REACTION OF 'S'H$^+$ IN MORE CONCENTRATED SOLUTIONS OF (1) SULPHURIC ACID, (2) NITRIC ACID, (3) BENZENESULPHONIC ACID

Initial concentration of 'S'H$^+$ = 0.100 *M*
Excess H$^+$ over that required to neutralize 'S' = 0.150 *N*
H$^+$ and Cl$^-$ required for complete reaction = 2.00 me.
Reaction temperature = 72° C.

	Time, hr.	Milliequivalents of		k, hr.$^{-1}$
		H$^+$ produced	Cl$^-$ produced	
(1)	0.5	0.076	0.068	—
	1	0.096	0.090	—
	2	0.160	0.148	2.45×10^{-2}
	6	0.268	0.260	1.85
	16	0.435	0.425	1.80
	23	0.602	0.570	2.40
	51	0.776	0.762	2.45
(2)	0.5	0.011	0.014	—
	1	0.030	0.028	—
	5	0.099	0.086	—
	10	0.180	0.200	1.60×10^{-2}
	17.7	0.228	0.300	1.57
	24	0.310	0.368	1.65
	47.5	0.495	0.500	1.66
(3)	0.5	0.035	0.040	—
	3.3	0.075	0.076	1.2×10^{-2}
	7	0.160	0.180	1.4
	21	0.306	0.292	1.2
	27	0.390	0.384	1.3

smaller (Tables I (2) and II (2)). The existence of a secondary reaction is equally pronounced when the excess of nitric acid is large as when it is small. The disappearance of hydrogen ion and nitrate ion are again equal. The values for k were very erratic at the higher temperatures.

The reaction of 'S'H$^+$ in benzenesulphonic acid at all experimental temperatures conforms to a rate equation of a type similar to that for the other acids, except that the correction factor for hydrogen ion production is 10^{5z} instead of 10^{10z}. The smaller correction factor may be due to the fact that this is the strongest acid used in these experiments, and the hydrogen ion formed during reaction is less effective in changing the pH of the solution.

The relative rates of hydrolysis of 'S'H$^+$ ion increase in the following order for the acids used; hydrochloric, benzenesulphonic, nitric, and sulphuric.

The relative rates of hydrolysis of 'S'H$^+$ ion in benzenesulphonic acid with various initial 'S'H$^+$ concentrations were studied. With a large excess of hydrogen ion and a low concentration of 'S' the reaction in its initial stages followed a first order rate expression. Under such conditions the concentration of hydroxyl ion was practically constant. Where the hydrogen ion produced from hydrolysis was comparable with the initial hydrogen ion excess, the first order rate decreased markedly as hydrogen ion was produced. It was noticed, however, that although the rates differed to a large extent, the hydrogen ion and chloride ion productions were about equal, which showed that little, if any, dimer formation occurred. An inhibiting effect of chloride ion when added in the form sodium chloride to the solution of low 'S' and low acid excess concentration was demonstrated.

TABLE III

DATA FOR CALCULATION OF ACTIVATION ENERGIES FOR THE RATE OF HYDROLYSIS IN VARIOUS ACID EXCESSES

Acid excess	Temp., °A	$1/T \times 10^{-3}$	*$k \times$ hr.$^{-1}$	$\log_{10}k$
0.030 *N* HCl	345	2.90	2.25×10^{-2}	$\bar{2}.35$
	373	2.68	3.0×10^{-1}	$\bar{1}.48$
	404	2.48	2.20	0.34
0.030 *N* HNO_3	345	2.90	5.00×10^{-2}	$\bar{2}.70$
	373	2.68	6.60×10^{-1}	$\bar{1}.82$
	402	2.49	5.50	0.74
0.150 *N* H_2SO_4	345	2.90	4.71×10^{-2}	$\bar{2}.67$
	373	2.68	8.30×10^{-1}	$\bar{1}.92$
	389	2.57	2.50	0.40
0.150 *N* HNO_3	345	2.90	1.62×10^{-2}	$\bar{2}.21$
	373	2.68	2.1×10^{-1}	$\bar{1}.32$
	389	2.57	9.0×10^{-1}	$\bar{1}.95$
0.150 *N* $C_6H_5SO_3H$	345	2.90	1.5×10^{-2}	$\bar{2}.18$
	353.5	2.83	4.3×10^{-2}	$\bar{2}.63$
	373	2.68	1.95×10^{-1}	$\bar{1}.29$
	389	2.57	1.20	0.08

* *These values for k are initial first order rate constants, uncorrected by the factor* 10^{10x}. *These data give approximately linear relations in an Arrhenius plot.*

TABLE IV

PARAMETERS IN THE EQUATION $k = Be^{-E/RT}$ FOR THE HYDROLYSIS OF 'S'H$^+$

Concentration of 'S'	Excess acid	k(rel) 100° C.	E, kcal.	$\log_{10}B$
0.084 *M*	0.03 *N* HCl	1	22	12.2
0.084 *M*	0.03 *N* HNO_3	2	23	13.2
0.100 *M*	0.15 *N* H_2SO_4	2	25	14.4
0.100 *M*	0.15 *N* HNO_3	1	25.5	14.2
0.100 *M*	0.15 *N* $C_6H_5SO_3H$	4	25.5	15.1

It has been noticed (Tables III–IV) that the energy of activation for the hydrolysis of 'S'H$^+$ is higher the larger the hydrogen ion excess. This may be due to an effect of the hydrogen ion on the energy of the C–Cl bond, acting through an influence on the nitrogen nucleus.

Discussion

It is quite apparent that hydrolysis of 'S'H$^+$ is not a simple process. Although essentially first order, constancy of the k values is marred by changes in reaction medium; rate constants calculated from the usual first order expression decrease rapidly as the reaction progresses. Both hydrogen ion and chloride ion have been noted to decrease the rate. Since both are formed during the course of hydrolysis, the k values may be expected to decrease during the course of the reaction. The factor 10^{10x} is empirical but it fits the experimental results closely.

There are four mechanisms possible for the hydrolysis reaction. The first two assume an acid–base equilibrium such that the reactant is of the tertiary nitrogen form. The third consists of a rearrangement of the 'S'H$^+$ ion to expel HCl and form an imine intermediate. The fourth involves a direct attack on the β-chlorines of the 'S'H$^+$ ion.

The first two possible mechanisms may be discussed together, keeping in mind the acid–base equilibrium existing in solutions of 'S' in water.

$$\text{'S'H}^+ \rightleftharpoons \text{'S'} + \text{H}^+$$

The constant for equilibrium is

$$K = \frac{[\text{H}^+]\ [\text{'S'}]}{[\text{'S'H}^+]}$$

The pK for 'S' has been found to be 6.1 (2,5) and the initial concentration of free 'S' in a system containing a slight excess of strong acid (pH 2) is therefore given by

$$\begin{aligned} \text{'S'} &= K \frac{[\text{'S'H}^+]}{[\text{H}^+]} \\ &= 1.2 \times 10^{-6} \times \frac{0.05}{0.01} \\ &= 6 \times 10^{-6} \text{ at } 25^\circ \text{ C.} \end{aligned}$$

At the temperatures at which the hydrolysis reaction was studied the value of ['S'] will probably be somewhat higher. However, the concentration of 'S' in the tertiary form is certainly very small and decreases with reaction forming more 'S'H$^+$ ion.

Hence, although free 'S' represents a very reactive state, it is unlikely that hydrolysis will proceed through the free 'S' to the exclusion of hydrolysis of the positive ion.

Bartlett's postulation for the hydrolysis of free 'S' in water (1) assumes free 'S' to undergo rapid iminization in pure water, followed by cleavage of the imine ring by water or hydroxyl ion to form products. This mechanism

accounts for the decrease in rate constants as hydrogen ion is produced, since reactant disappears by a reaction other than hydrolysis. However, it has been shown that the imine ring is quite stable to water (9), and it is unlikely therefore, that hydrolysis takes place through the imine intermediate.

The third possible mechanism is the simultaneous expulsion of H^+ and Cl^- from an activated '$S'H^+$ ion to form an imine ring. Even admitting such a possibility the imine ring has been found quite stable to water.

The fourth and probable course of reaction involves a direct attack on the β-chlorines by hydroxyl ion.

To react, a molecule must have a definite amount of energy, acquired by successive collisions with other molecules in the system. Once this critical energy state has been reached the molecule is considered to exist as an activated complex. In this latter state it may lose energy to form products, or revert to reactants.

This concept enables the hydrolysis of '$S'H^+$ to be represented by a scheme of the type.

$$OH^- + R^+Cl \longrightarrow \left[R^+ \begin{matrix} OH^- \\ Cl \end{matrix}\right] \qquad A$$

$$R^+OH \ldots . Cl^- \qquad B$$

$$R^+OH + Cl^- \qquad C$$

where R^+ represents the '$S'H^+$ ion except one β-chlorine.

Hydroxyl ion collides with RCl to form an activated complex, A. This complex assumes a stable product configuration represented by R^+OH and Cl^- as represented in B and C. This mechanism makes allowance for the effect of OH^- and Cl^- retardation. The effect of hydroxyl ion is obvious from mass law considerations. The effect of chloride ion is not as evident, but it seems reasonable to assume either Stage A or Stage B may be reversed by chloride ion, thus inhibiting formation of product.

With large acid excess, the energy of activation of hydrolysis is greater than at low acid excesses. This is believed due to the influence of the anion. Since the particle undergoing hydrolysis is a positively charged ion, it is not unlikely that the anions of the acid take up positions surrounding the '$S'H^+$ ion. This negative layer surrounding the reactant should require the OH^- ion to have extra energy to penetrate the ionic layer and collide with the '$S'H^+$.

Once favorable collision has been established between the hydroxyl ion and the '$S'H^+$ ion to form the activated complex, this ionic sheath serves to aid in the stabilization of the products. It serves to prevent the interference of choride ion to reverse the reaction to the extent found in small acid excesses. The charge on the ion apparently makes little difference, but a relatively higher value of the parameter B in the Arrhenius relation has been noted for benzenesulphonic acid. This is perhaps due to the size of the anion, which serves to form a denser layer about the '$S'H^+$ ion and reduce the collisions of chloride ion with the activated complex. This stabilizing effect of the anions should manifest itself as an increase in the B factor.

No account has been taken of the difference between the hydrolysis of 'S'H$^+$ and 'S'H$^+$–chlorohydrin. Analytically it was impossible to determine from which compound the measured hydrolysis products originated. However, in the hydrolysis of bis-β-chloroethyl sulphide (4) the second displacement of chlorine is actually much faster than the first.

Comparison of the mechanisms suggested for the hydrolysis of dimer and 'S'H$^+$ ion would seem to be unjustified. The experimental data indicate that the mechanisms of the two reactions cannot be similar since the hydrolysis of the dimer is independent of pH in the lower range and not greatly affected by chloride ion, while the hydrolysis of 'S'H$^+$ ion is retarded by both hydrogen ion and chloride ion. Moreover, the activation energy for hydrolysis of the dimer is 29.7 kcal., while that for hydrolysis of 'S'H$^+$ is only 23 to 25.5 kcal.

References

1. BARTLETT, P. D. Private communication.
2. HANBY, W. E., HARTLEY, G. S., POWELL, E. O., and RYDON, H. N. J. Chem. Soc. 519. 1947.
3. MARION, L. Private communication.
4. MOELWYN-HUGHES, E. A. Private communication.
5. OGSTON, A. G. Private communication.
6. ROBINSON, D. Private communication.
7. SCOTT, W. W. (editor). Standard methods of chemical analysis. Vol. 2. 4th ed. D. Van Nostrand Company, Inc., New York. 1925.
8. THOMPSON, A. L., HARDWICK, T. J., HAY, A. W., and WINKLER, C. A. Can. J. Research, B, 26 : 161. 1948.
9. THOMPSON, A. L., HARDWICK, T. J., and WINKLER, C. A. Can. J. Research, B, 26 : 181. 1948.

The authors wish to acknowledge the assistance of the Defence Research Board in procuring the information referred to as 'Private communication'.

LOW TEMPERATURE, LOW PRESSURE FRACTIONATION NATURAL GAS[1]

By E. H. Boomer,[2] A. Gillies,[3] and J. T. Hugill[4]

Abstract

A simple inexpensive apparatus was devised that could be used to carry out routine analyses of small samples of natural gas, or similar mixtures of lower boiling hydrocarbons, with an accuracy of 0.1% or better. The apparatus operates at low temperatures and pressures and can fractionate as little as 60 cc. A complete analysis takes about two and one-half hours and consumes 3 lb. of liquid air.

Introduction

In connection with the phase equilibrium work proceeding in these laboratories it was necessary to employ some means of analysis of the gaseous phase. Principal interest was attached to the content of lighter hydrocarbons from methane through to pentane, and nitrogen. In the process of removing the phase samples, a primary separation was made into a gas consisting of pentane and lighter hydrocarbons and a liquid consisting of pentanes and heavier hydrocarbons. This separated gas had to be analyzed into its component parts with a precision comparable with other measurements. Further, in view of the number of such analyses, a relatively simple, rapid, and inexpensive method was desirable. The development and application of a new fractionating column for analysis of hydrocarbon gas mixtures by fractional distillation at low pressure will be described in this paper.

Using the basic methods of Shepherd, Ward (7) devised an improved apparatus that cuts the analysis time to about three hours, and gives results comparable in accuracy with those of Shepherd. Ward also employs a train of condensers—five in number—which are kept accurately at certain temperatures by the use of liquid air baths and electric heaters. By varying the temperature gradient over four of the condensers and keeping the fifth at liquid air temperature, separation is effected at pressures of less than 1 mm. of mercury. Ward's method possesses considerable advantages over previous work. It shortens the time of analysis required by Podbielniak and Shepherd, uses much less liquid air, and is satisfactory with small gas samples of the order of 100 cc. The accuracy of the method is comparable with that obtained by Shepherd.

Von Elbe and Scott (3) have applied low temperatures and pressures to the fractionation of liquids having almost identical boiling points at atmospheric pressure. The procedure involves no reflux and consists mainly of

[1] *Manuscript received August 6, 1947.*

Contribution from the Chemical Laboratories of the University of Alberta, Edmonton, Alberta, with financial assistance from the National Research Council of Canada.

[2] *Deceased.*

[3] *Present address: Research Laboratories, Dominion Rubber Co. Ltd., Guelph, Ont.*

[4] *Present address: Development and Engineering Dept., Canadian Liquid Air Co., Montreal.*

drawing a sample of less than 0.1 cc. through a temperature gradient at a slow uniform rate. A separation of *p*- and *m*-xylenes to within a few per cent is reported by the authors.

The use of low temperatures and pressures and the omission of a long fractionating column, reflux, and a large sample, depends on two well known principles. At low temperatures, the vapor pressure ratios of successive members of a hydrocarbon series increase greatly, and almost complete separation is possible in simple fractionating apparatus.

The original attempts at fractionation of complex gaseous mixtures were carried out by Ramsay and Travers (5). They studied the gaseous elements of the atmosphere by condensing samples of air at low temperatures and effecting separation by repeated distillations and condensations at low pressures. Burell, Seibert, and Robertson (2), using a modification of Ramsay's work, developed the first apparatus and methods for the fractional distillation of natural gas. The apparatus was complicated and the procedure tedious and time-consuming. Further, slow combustion analysis had to be made to separate the binary mixtures obtained from the fractionation.

Shepherd and Porter (6) improved on Burell's methods by employing a series of condensers and pumps and repeated distillations and condensations. The methods and apparatus are an improvement on previous work in that the operation is somewhat shorter and separation is obtained with a high degree of accuracy.

Podbielniak (4) devised a method employing a conventional fractionating column of high efficiency working at low temperatures and at pressures from atmospheric to 100 mm. of mercury. His apparatus possesses the advantage over previous apparatus in that the time is considerably shortened for a complete analysis. The limit of accuracy is, however, reduced to that of engineering calculations.

TABLE I

VAPOR PRESSURE RATIOS

Hydrocarbons	−175° C.	−160° C.	−150° C.	−140° C.	−120° C.	−100° C.
Methane–ethane	2000	450				
Ethane–propane		66	39			
Propane–*i*-butane			16.5	5.5		
Propane–*n*-butane			18.2	18.3		
n-Butane–*i*-pentane					6.2	1.8
i-Butane–*i*-pentane					25.0	6.3

Table I shows the ratios of the vapor pressures of successive members of the paraffin hydrocarbon series at several temperatures above that of liquid air, obtained from data in the I.C.T. and extrapolated to lower temperatures.

In addition to the increased vapor pressure ratios the actual amount of the vapor phase over the liquid phase is small at reduced temperatures, and hence

a negligible amount is left at the completion of each distillation. Further, the small volumes of liquid and gas phase and the relatively large surface of contact permit rapid establishment of equilibrium conditions.

Employing essentially the same ideas used by Ward, apparatus was devised that combines his condenser train into one fractionating column and a liquid air trap. The apparatus and methods devised possess several advantages over Ward's set up.

Materials

Prior to the fractionation of unknown samples, several synthetic mixtures were prepared in order to determine the best operating conditions for the column, and to develop a technique in using it. To make up these synthetic mixtures in somewhat the same proportions and containing the same constituents to be met with in the solubility work, it was necessary to obtain samples of methane, ethane, propane, *n*-butane, and *i*-butane in as pure a state as possible.

Methane was prepared from Viking gas, which in itself contains 95% of this hydrocarbon. The gas was admitted to the analytical apparatus (Fig. 1) and passed through condensers *B* and *C*, 25 cc. of liquid being condensed. Condenser *C* was kept at −165° to −170° C. and *B* at liquid air temperature. Noncondensable gas was removed by repeated evacuation to a pressure of 5 cm. of mercury. The liquefied material was allowed to evaporate, the first and last thirds being discarded. The material retained was distilled and again the first and last portions were discarded, and the middle third retained and transferred to a storage bulb. Density determinations were made on the stored gas and it was found to have a density of 0.7183 gm. per liter at 0° C. and 76 cm. of mercury pressure. The density of methane as given by the I.C.T. is 0.7168 gm. at 0° C. and 76 cm. of mercury pressure. Precision combustion analysis showed no higher hydrocarbons, any impurities present being traces of nitrogen.

Ethane was prepared by the Grignard reagent method. The reagent was prepared by treating ethyl bromide in anhydrous ether solution with magnesium wire. Crystalline iodine was added as a catalyst. The reagent was then hydrolyzed to give ethane. The gas produced was passed through a water condenser, a trap surrounded by ice and water, and then a coil immersed in a freezing mixture of ice and salt. This removed nearly all the ether carried over with the ethane. To remove the last trace of ether, the gas was bubbled slowly through fuming sulphuric acid followed by a 10% solution of potassium hydroxide to remove sulphur trioxide. The gas was then passed to a small gasometer. Tests on the gas indicated that a small quantity of unsaturated hydrocarbon was present, so all the gas was passed through a saturated solution of bromine water followed by potassium hydroxide solution. It was then dried by passing it over phosphorus pentoxide and transferred to the analytical apparatus (Fig. 1).

Using liquid air and repeatedly distilling the gas back and forth between two condensers and discarding the first and last quarters, a sample was obtained that had a density of 1.3569. This may be compared with the figure 1.3535 given by Beattie, Hadlock, and Poffenberger (1). Precision combustion analysis showed a carbon–hydrogen ratio in the gas of 3.33.

Propane was obtained from a cylinder of the commercial grade 98% gas purchased from the Carbide and Carbon Chemicals Company. The gas was condensed in Condenser *A* (Fig. 1) at 160° C. until a liquid sample of about 20 cc. was obtained. This sample was vaporized and 3 cc. discarded. The temperature of Condenser *A* was raised to −100° C. and Condenser *B* was kept at −143° C. The Toepler pump was operated till the pressure was 0.1 mm. The sample was then vaporized from *A* and condensed in *B*, portions of the gas being pumped off frequently. The temperatures of the condensers were again adjusted, and the system pumped down to 0.05 mm. of mercury for one-half hour. The sample was then vaporized and pumped to a storage bulb. Its density was found to be 2.0021 gm. per liter at 0° C. and 76 mm. of mercury pressure. This may be compared with the value 2.020 as given in the I.C.T.

n-Butane and *i*-butane of approximately 99.57% purity were obtained in cylinders from the Ohio Chemical and Manufacturing Company. Approximately 25 cc. of each gas, as liquid, was condensed in Condenser *A* at −80° C. This sample was distilled and the first 10 and the last 5 cc. were discarded and the middle 10 cc. was vaporized and pumped to the storage bulbs after density determinations had been made; successive readings of the vapor pressure at this temperature gave a constant value comparable with that recorded in the I.C.T. The density of *n*-butane was 2.6685 gm. per liter and of *i*-butane 2.6467 gm. per liter at 0° C. and 76 cm. of mercury pressure compared with the value of 2.673 for *i*-butane given by the I.C.T.

It should be pointed out that relatively few values of density for the gaseous paraffins except methane are available and agreement is poor amongst them. The materials prepared here are believed to be of high purity because of unchanging density and vapor pressure upon distillation.

Apparatus

A detailed drawing of the fractionating column is shown to scale in Fig. 2 and a conventional drawing showing the associated apparatus appears in Fig. 1.

Preliminary experiments with a small column of glass showed that excellent heat transmission and a controlled temperature gradient from top to bottom of the column were necessary. In order to achieve these requirements, the column was made entirely of metal and of small size. Further, it was designed to be used in an inverted position, what may be called the still being at the top, while the vapor offtake is at the bottom.

To maintain a desired temperature gradient over the column, when completely within a Dewar tube containing a refrigerant such as liquid air, it was

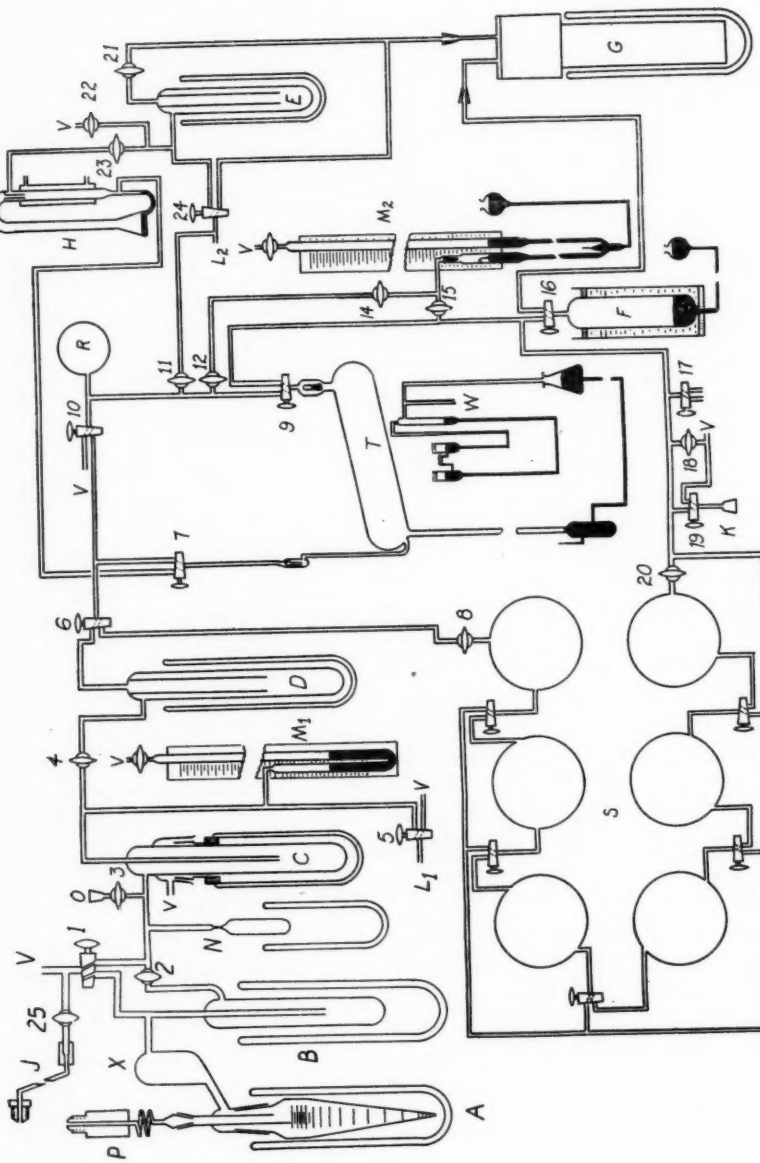

G
21
E
22
V
23
H
24
L_2
V
M_2
14
15
16
F
R
11
12
9
T
W
17
V
18
19
K
10
V
7
6
8
20
D
4
V
M_1
5
V
L_1
C
3
0
V
1
V
N
2
25
J
X
B
P
A
S

FIG. 1.

obviously most practical to have the temperatures decreasing from the top to the bottom. In addition to the simplicity of construction, the advantage is gained that heat transmission is confined largely to the column itself and there is little heat transfer by convection in the atmosphere surrounding the column.

The column consists of a core, outside tube, and top and bottom heaters. The core was machined from a brass rod, circumferential grooves $\frac{1}{8}$ in. wide and $\frac{1}{4}$ in. deep being cut over its full length in such a way as to leave $\frac{1}{16}$ in. thick plates appearing to be strung on a central rod. A shallow segment was cut from each plate but on opposite sides successively up the column. The core was bored along its axis over the full length to provide a vapor offtake tube from the bottom of the column. The core was tinned and, while hot, inserted into a tinned brass tube serving as the outer wall of the column. Upon cooling, the core and tube formed a substantial unit, the plates with segments removed to permit flow of vapor acting the part of the fractionating column of relatively large surface and long vapor passage.

A brass outlet tube was threaded and sweated into the top of the core and communicated with the central hole. A second brass tube, the inlet tube, was attached to the core in the same manner and communicated with the upper plate. These tubes, which serve to support the weight of the column from the cover plate, *E*, and terminate in the standard taper ground joints, *M*, are a principal source of heat entry and should be made of German silver or a similar alloy of low thermal conductivity. They were insulated with cotton wool for some distance above the plate *E*.

FIG. 1.

The bottom of the column was closed by a brass plug into which a thermocouple well was machined of such length that the thermocouple was within $\frac{1}{8}$ in. of the beginning of the vapor offtake tube. Three other thermocouple wells were inserted through the sides of the column about 2 in. apart as shown. A fifth thermocouple well was drilled into the top of the core. This well terminated near the top plate. This number of thermocouple wells was necessary to the development of the column and served to show the temperature gradient along its length.

In another column, with slight changes in design, experience has shown that only two thermocouples are essential, although four would be convenient.

Brass tubes each machined with a double thread 16 to the inch were sweated on to the bottom two inches and top two inches of the column. These were coated with shellac, baked, and a double silk covered 30 gauge manganin wire was wound in a parallel loop in the threads. Copper leads were soldered to the ends of the manganin and passed up the side of the column to terminals on the plate *E*. The bottom assembly was wrapped in lead foil and a split spring-brass tube fitted over the foil to produce good metallic contact from the inside of the column to the outside of the outer tube. The upper coil was left exposed, being surrounded by a tube $\frac{1}{8}$ in. larger in diameter and closed at the top and bottom by bakelite disks. These two assemblies served as

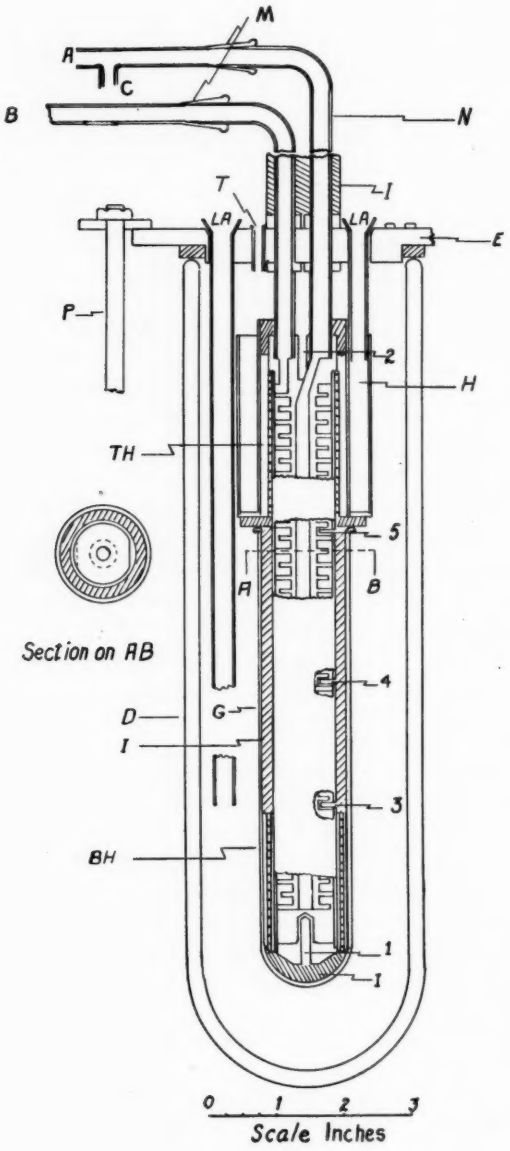

M
A
C
B
N
T
I
LA
LA
E
P
2
H
TH
5
A
B
Section on AB
4
D
G
I
3
BH
1
I
0 1 2 3
Scale Inches

FIG. 2.

heaters, the current being controlled by Variac transformers using 24 v. a.c. in their primary circuits.

Surrounding the upper heater and $\frac{1}{4}$ in. away from it was an annular brass cup as shown. It served as a liquid air container for control of the top temperature and as a means of cooling the top of the column quickly without raising the liquid air level in the Dewar flask above the bottom heater.

The column above the lower heater and below the top heater was wrapped with insulating material and a close-fitting glass tube *G* closed at the bottom end was slipped on. A layer of infusorial earth, about $\frac{1}{8}$ in. thick in the bottom of the glass tube, protected the brass closure plate and the thermocouple at the bottom of the column from too direct exposure to liquid air temperature. This insulation was in effect the equivalent of the heater assembly in controlling heat transfer, and was found essential in the production of uniform temperature over the bottom portion of the column.

Thermocouple leads were passed up the column under the insulation to terminals on the bakelite coverplate *E*. This plate was supported by three steel rods attached to the bench below. The holes *LA* through the plate *E* were for the introduction of liquid air, via glass tubes, as shown. One led to the annular cup at the top of the column and the other led to, and terminated at, the top of the bottom heater. A Dewar flask, *D*, supported on an adjustable pillar (not shown) surrounded the column and its top was fitted through an insulating gasket to the lower face of the plate *E*, when in the operating position. In order to keep the plate *E* free from ice and water, a gentle stream of air was blown across it continuously. This was found necessary to keep the plate *E* at a reasonably constant temperature as it was used as the cold junction for the thermocouples.

Leads from the heater terminals on plate *E* were made to the source of current and from the thermocouple terminals to a multiple point rotary switch, so that the voltages and hence temperatures could be determined quickly on one potentiometer. The correction for the cold junction at plate *E* was determined by means of a thermocouple on the plate surface, whose other junction was in an ice-water mixture.

Procedure and Results

Preliminary to carrying out a fractionation, the column, connecting tubes, and accessory apparatus were evacuated (Fig. 1). Mercury was allowed to fill the sample burette *F* and to rise about $\frac{3}{4}$ in. above stopcock 16 in the tube through which the sample passes to the column. Stopcock 16 was reversed, the mercury lowered to the mark etched at the bottom of the sample burette, and the pressure and the temperature of the gas sample recorded.

With stopcocks 24 and 21 closed, the temperatures along the column were adjusted to the values required for the separation of methane, as shown in Table V. The level of liquid air was maintained at the top of the bottom heater and small additions to the top liquid air cup were made from time to

time. Stopcock 16 was again reversed, and slightly opened to the column. The gas bubbled through the mercury; this indicated qualitatively the rate at which it was entering the column. An enlargement in the tube, a few inches above the stopcock, prevented the mercury from being carried over into the column. The gas was permitted to enter slowly, as no fractionation took place otherwise.

With stopcock 23 closed, the trap *E* was cooled with liquid air and stopcock 21 slightly opened until the pressure was equalized. Stopcock 24 was slightly opened to McLeod gauge L_2 and the pressure again equalized. Stopcocks 21, 23, and 24 were then fully opened and the gas pumped off with the Toepler pump, *T*, until the pressure in the column read 1 mm. The diffusion pump, *H*, was then operated in conjunction with the Toepler until the pressure remained constant at 0.25 mm. of mercury. The amount of methane and nitrogen was measured in the fraction receiver, *R*, by means of the manometer, M_2. Owing to the small mass of gas in each fraction it was found impractical to determine the nitrogen content of the first, or methane–nitrogen fraction, by means of density determinations. Combustion in the Orsat apparatus was therefore resorted to.

With stopcocks 21 and 23 closed the temperatures along the column were adjusted for ethane (see Table III), then stopcock 21 was opened and the gas distilled over into the liquid air trap, *E*. When the McLeod gauge showed a pressure of 0.10 mm. of mercury in the column, for three successive readings with stopcock 21 closed, distillation was discontinued. The liquid air was removed and the ethane pumped off with diffusion pump *H* and Toepler pump *T* and measured. The same procedure was repeated for each of the heavier gases after the correct temperature distribution had been established in the column.

After the butanes had been removed and measured, the column was allowed to warm up and the pentanes plus any heavier hydrocarbons pumped off and measured as vapor. The amount of pentanes plus was generally very small, and frequently the McLeod gauge was used to read the pressure in the fraction receiver.

To complete one run required about two and one-half hours for a lean gas and three hours for a rich gas. Liquid air consumed per run averaged about 3 lb.

In the development of the technique of operation with the column the primary variables observed and adjusted were the temperatures, as measured by the five thermocouples, and the pressure on the outlet side of the column, as measured by the McLeod gauge. In addition, the pressure in the fraction receiver showing the process of distillation was of importance in development work using mixtures of known composition. The work of Ward in determining suitable cut temperatures for his apparatus was of great value in providing a guide to be followed in fixing the lowest or vapor offtake temperature.

The procedure adopted in testing the column was to set the vapor offtake temperatures, i.e., *TC* 1, at the temperatures listed by Ward for the fourth

fractional condenser in his train. Attempts were made to maintain the top of the column, i.e., *TC* 2, at the temperature given by Ward for his first condenser. This was not possible and also found to be unnecessary. In practice, it was found necessary only to maintain *TC* 5 somewhat below the temperature set by Ward for his first receiver, and *TC* 2 the same or warmer. The result was a satisfactory temperature gradient down the column to the fixed bottom temperature.

After some experience with the column on mixtures of known composition, and some minor adjustments, the following results were obtained.

TABLE II

Gas	Volume per cent			
	Mixture No. 3 as prepared	Found		
		1	2	3
Methane	53.73	53.43	53.56	53.70
Ethane	24.21	24.36	24.14	24.29
Propane	13.53	13.36	13.40	13.62
Butanes	8.53	8.85	8.90	8.39
Gas	Mixture No. 4 as prepared	Found		
		1	2	
Methane	48.25	48.17	48.21	
Ethane	21.71	21.92	21.77	
Propane	12.15	12.06	12.12	
Butanes	17.89	17.85	17.90	

The following typical duplicate analyses of three rich and three lean gases, after the technique for operation had been well developed, are shown in Table III. These results indicate the accuracy that can be obtained on a variety of gases of different compositions.

TABLE III

	Duplicate analyses of rich and lean gas mixtures, volume %											
	Rich Gas						Lean Gas					
Gas No.	1		2		3		4		5		6	
Analysis No.	1	2	1	2	1	2	1	2	1	2	1	2
Methane + N_2	62.40	62.40	54.60	54.67	64.72	64.71	93.30	93.29	92.08	92.03	93.30	93.29
Ethane	17.93	17.90	16.69	16.77	17.66	17.67	4.86	4.86	5.77	5.77	4.86	4.86
Propane	12.64	12.76	15.25	14.96	11.81	11.82	1.25	1.28	1.56	1.52	1.25	1.28
Butane	6.13	6.05	12.98	12.97	5.71	5.71	0.45	0.46	0.48	0.64	0.45	0.46
Pentanes	0.90	0.89	0.48	0.63	0.10	0.09	0.14	0.11	0.11	0.10	0.14	0.11
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

The results given below on the analysis of Royalite Gas at periods of several months apart are an indication of the reliability of the analysis and technique.

TABLE IV

	Vol. % as at Dec. 1/39	Vol. % as at Mar. 25/40
Methane	84.74	84.62
Ethane	9.35	9.44
Propane	4.03	4.05
Butane	1.56	1.58
Pentanes	0.32	0.31
	100.00	100.00

The cutting pressures used at all times were those set by Ward. These were 0.25 mm. of mercury for methane, and 0.10 mm. of mercury for all other gases. Cutting temperatures for the fractions are listed in Table V, together with the number of the thermocouple. The temperatures, in degrees Centigrade, are those at which separation of the individual component from the rest of the gas takes place.

TABLE V

Gas	*TC* 1	3	4	5	2
Methane + N_2	−175	−169	−164	−150	−119
Ethane	−160	−154	−145	−135	−109
Propane	−142	−134	—	−120	−100
Butane	−117	—	—	−100	− 74

Thermocouples 3 and 4 were used to check the temperature gradient during the calibration of the column and were seldom used afterwards. Thermocouple No. 3 is very useful, however, in following the initial cooling of the column and should be retained. Owing to the construction of the column, the changes in temperature at the top were greater and less readily controlled than at the bottom points. Variations up to 10° C. in the temperature of *TC* 2 did not, however, affect the results of fractionation as long as *TC* 5 was maintained close to the temperature listed, a requirement easily achieved. Thermocouple No. 4 could be discarded without loss. For the methane plus nitrogen cut, the temperature of *TC* 1 could be between −172° and −175° C. The other cut temperatures and the temperature of *TC* 5 as listed were maintained to within 1° C.

A few attempts were made to separate *n*-butane and *i*-butane but without success. As such a separation was not required in connection with the work, no further attempts were made to effect this separation. The small vapor

pressure ratio of the butanes at the temperatures used (see Table I) makes it highly improbable that the present technique will suffice.

It should be pointed out that no separation of nitrogen and other non-condensable gases from methane was attempted. Orsat analysis of the methane fraction provided the information desired. However, it is quite probable that a separation in the column can be made. The apparatus and method may be adapted easily to hydrocarbon mixtures with other common gases when used in conjunction with an Orsat apparatus. If olefins are present, they may be removed with the corresponding paraffin and determined by absorption in the usual way.

Discussion

The results given are not exceptional in any way and have been repeated many times on a variety of gas mixtures. The close agreement between duplicate analyses as illustrated here is superior to that obtained in other methods of analysis with the possible exception of that used by Ward.

The dependence to be placed on the results is illustrated in the discussion of the development of the method by analysis of gas mixtures of known composition. The agreement found there is as good as the accuracy with which the known mixtures were made. The slightly better agreement among duplicate analyses suggests that they give a truer analysis of the mixtures.

The analyses were calculated on the basis of the sum of the volumes of all the components taken off and not on the volume of sample initially taken. The total volume taken off, calculated to the input pressure of the sample was always slightly larger than the actual input volume, usually 0.2 to 0.4% larger. The sample was measured at about 60 cm. of mercury pressure and the fractions taken off at 30 cm. of mercury or less. The discrepancy between the sample volume and the total volume taken off may be wholly accounted for by the deviation of the initial sample from the ideal gas laws. The fractions were measured under more nearly ideal conditions and hence the analyses, as calculated, are close to molecular percentages.

As a result of present experience, several problems arise which may be solved by modifications in a future design. Considerable trouble was experienced in the initial cooling of the column to the temperatures required for methane separation. This may be due partly to heat losses which can be reduced by using German silver inlet and outlet tubes and dispensing with the air space between the top heater and the annular liquid air cup. As was pointed out in the procedure, only four thermocouples were necessary, and *TC* 4 can be dispensed with.

Summarizing the performance of the apparatus and the value of the method in the analysis of mixtures of gaseous paraffin hydrocarbons, we may mention the following points:

1. The time required for one analysis is exceptionally short, approximately 2.5 hr.

2. The liquid air consumed per analysis is low, approximately 3 lb.
3. A small gas sample, usually 85 cc. but ranging from 50 to 150 cc. more or less, is sufficient for a precise analysis.
4. The apparatus is relatively simple, inexpensive, and the technique of operation readily learned.
5. The results are highly accurate, analysis in duplicate agreeing to 0.05% in lean gases and 0.1% in rich gases.

References

1. BEATTIE, J. A., HADLOCK, C., and POFFENBERGER, N. J. Chem. Phys. 3 : 93. 1935.
2. BURELL, G. A., SIEBERT, F. M., and ROBERTSON, I. W. U.S. Bureau of Mines Technical Paper 104. 1915.
3. ELBE, G. VON and SCOTT, B. B. Ind. Eng. Chem., Anal. Ed. 10 : 284. 1938.
4. PODBIELNIAK, W. J. Ind. Eng. Chem., Anal. Ed. 3 : 177. 1931.
5. RAMSAY, W. and TRAVERS, M. W. Experimental study of gases. Macmillan and Co., London. 1901.
6. SHEPHERD, M. and PORTER, F. Ind. Eng. Chem. 15 : 1143. 1923.
7. WARD, E. C. Ind. Eng. Chem., Anal. Ed. 10 : 169. 1938.

A RHEOLOGICAL STUDY OF SOLUTIONS OF NITROCELLULOSE[1]

By David Fensom[2] and J. H. Greenblatt[3]

Abstract

By using a MacMichael viscometer the change in viscosity at various rates of shear was determined for solutions of various types of nitrocellulose in the solvents; acetone, *n*-butyl acetate, Hercules' mixed solvent, and dibutyl phthalate. It was found that all solutions of low intrinsic viscosity nitrocellulose were dilatant in dilute solution, while those of high intrinsic viscosity were thixotropic. Thixotropy also changed with concentration, the solutions studied going from dilatant to thixotropic through Newtonian types on increasing the concentration. Thixotropy and dilatancy were both found to decrease as the temperature increased. At a given concentration, both the viscosity and the structural viscosity of solutions varied with solvent, dibutyl phthalate giving both the highest viscosity figures and the greatest effect on structural viscosity.

It is well known that the physical properties of high polymer materials are dependent on their past history as well as the conditions of experiment. This is particularly true of the rheological properties of polymers and polymer solutions. Thus, in order to obtain a reasonably complete picture of the rheological properties of such materials when in the form of gels or suspensions, it is necessary to consider the effects of past history, concentration of polymer, effect of solvent, and the effect of velocity gradient. The action of these variables on the rheology of polymers and polymer solutions has been discussed in three recent reviews on the subject (10, Chaps, 1, 4, and 5; 11, Sec. I; 12, Chap. IX), and it can be concluded that for even a qualitative picture of the behavior of gels and colloid solutions of nitrocelluloses, the effect of these variables must be considered.

Experimental

The various samples of nitrocellulose under examination were tested for intrinsic viscosity and nitrogen content according to the standard methods. The intrinsic viscosities were measured at 0.05% concentration in *n*-butyl acetate after careful regulation of temperature, light, and time conditions. The intrinsic viscosity $[\eta]$ was taken as being very nearly $\frac{\ln (\eta_{rel})}{C}$. The duPont nitrometer was used to obtain nitrogen contents.

Although precautions were taken with the intrinsic viscosities to avoid light and to maintain constant temperature for 14 days in solution, the same accuracy is not claimed for the solutions of nitrocellulose tested with the MacMichael viscometer. In this case the solutions were made up, shaken for 15 min. every day until they were completely uniform in appearance.

[1] *Manuscript received July 30, 1947.*

Contribution from the Canadian Armament Research and Development Establishment, P.O. Box 1427, Quebec, P.Q.

[2] *At present, Ridley College, St. Catharines, Ont.*

[3] *At present, Graduate Student, Department of Chemistry, McGill University, Montreal, P.Q.*

The solutions were then poured into the viscometer up to the correct height. As the same cup, rotating disk, and height of liquid were used throughout the tests, these factors are included in the standardization constant.

Standard torsion wires were used, but each wire was calibrated against liquids of known viscosity, either distilled water or oils obtained from the U.S. Bureau of Standards.

The MacMichael viscometer was read in degrees. These were converted into absolute units by applying the standardization constant of each wire. The viscosities at different rates of shear are given in Table I. (Details of past

TABLE I

THE RATE OF SHEAR–VISCOSITY CHANGES OF NITROCELLULOSE SOLUTIONS

Nitrocellulose Reference No.	Rate of shear, r.p.m.	Viscosity at 20° C. in centipoises (concentration shown in upper left)							
		Hercules' solvent		*n*-Butyl acetate		Acetone		Dibutyl phthalate	
13	10	5.00%	4.90	5.00%	6.4				
	20		5.82		7.0				
	30		6.36		8.0				
	40		7.90		9.0				
12	10	5.00	167	5.00	500				
	20		167		460				
	30		168		450				
	40		—		444				
36	10			5.00	137				
	20				128				
	30				126.5				
	40				122				
30	10			5.00	118				
	20				116				
	30				116				
	40				116				
19	10	5.00	2.95	5.00	7.02	5.00	3.04	2.00%	86.0
	20		3.38		7.81		3.71		87.8
	30		4.31		8.61		4.10		88.0
	40		4.03		8.77		4.21		86.3
6	10	5.00	50.3	5.00	8.85				
	20		66.2		8.66				
	30		77.8		9.47				
	40		85.0		10.2				
32	10			5.00	6.96				
	20				6.79				
	30				7.25				
	40				7.83				
38	10			5.00	83.0				
	20				83.5				
	30				83.6				
	40				81.2				
34	10			5.00	427				
	20				463				
	30				462				
	40				454				

TABLE I—*Concluded*

THE RATE OF SHEAR–VISCOSITY CHANGES OF NITROCELLULOSE SOLUTIONS—*Concluded*

Nitrocellulose Reference No.	Rate of shear, r.p.m.	Viscosity at 20° C. in centipoises (concentration shown in upper left)							
		Hercules' solvent		*n*-Butyl acetate		Acetone		Dibutyl phthalate	
2	10	5.00	299	5.00	1350	5.00	133	1.00	104
	20		299		1340		137		103
	30		299		1310		136.5		92.6
	40		305		1255		136		96.0
9	10	5.00	3800	5.00	3800				
	20		3460		3400				
	30		3260		3300				
	40		3130		3100				
4	10	5.00	74000	1.00	80.3				
	20		62500		83.6				
	30		50600		84.5				
	40				84.4				
33	10			1.00	131				
	20				122				
	30				118.5				
	40				115.5				
5	10			1.00	1032	2.00	3380	0.50	2670
	20				805		2700		1970
	30				687		2290		1620
	40				613		2010		1370
28	10			5.00	1270				
	20				1250				
	30				1180				
	40				1130				
1	10	5.00	11600	5.00	3840				
	20		10500		3060				
	30		10000		2740				
	40		9200		2400				
35	10			5.00	1320				
	20				1232				
	30				1212				
	40				1170				
20	10	5.00	634	5.00	1090				
	20		572		1108				
	30		610		1090				
	40		605		1058				
29	10			1.00	75.1				
	20				78.9				
	30				73.1				
	40				67.7				
26	10			1.00	68.1				
	20				68.7				
	30				69.2				
	40				67.0				
39	10			5.00	3530				
	20				3030				
	30				2780				
	40				2630				

history of the nitrocellulose are given separately in Table II.) Four different solvents shown in the table; viz., acetone, *n*-butyl acetate, dibutyl phthalate, and the Hercules' mixed solvent (toluol 55%, ethyl alcohol 25%, ethyl acetate 20% by volume) were used to dissolve the nitrocellulose.

TABLE II

PROPERTIES OF NITROCELLULOSE SAMPLES USED IN PRESENT WORK

Nitrocellulose Reference No. N/C	Trade name N/C	Raw material	Industrial nitration process	Nitrogen, %	Intrinsic viscosity in *n*-butyl acetate $[\eta]$
13	AS ¼ sec.	Linters	*M*	10.65	0.54
12	AS ½ sec.	"	*M*	10.62	2.48
36	Low soluble	"	*D*	10.89	3.63
30	LL 55	"	*M*	11.36	2.76
19	RS ¼ sec.	"	*M*	11.63	0.68
6	RS ¼ sec.	Viscose	*M*	11.86	0.90
32	HX 8–13	Linters	*M*	11.96	1.07
38	HL 120–170	"	*M*	12.02	2.17
34	HM 15–20	"	*M*	12.15	2.49
2	RS 70	"	*M*	11.94	3.07
9	RS —	"	*M*	12.07	4.45
4	RS —	"	*M*	11.83	5.85
31	HH 5–15	"	*M*	12.23	5.90
33	Blasting	Cops	*A*	11.99	7.12
5	Blasting	Linters	*M*	12.28	10.6
28	—	"	*D*	12.24	2.51
1	Propulsive soluble	Wood pulp	*D*	12.28	3.75
35	Pyro	Linters	*M*	12.63	3.05
20	—	Wood pulp	*M*	12.58	3.51
29	—	Waste	*D*	13.11	4.68
26	—	Wood pulp	*D*	13.16	4.79
39	—	Linters	*M*	13.42	3.23

Raw material; cotton, except where mentioned.
Nitration method; A—Ardeer process.
M—Mechanical dipper process.
D—Displacement process.

Results

The complete range of nitrocellulose samples is recorded in Table I, in order to compare the effect of different solvents on thixotropy. The table is arranged in groups of related nitrogen contents; within each group the samples are given in order of increasing intrinsic viscosity. It may be seen that nitrocelluloses of low intrinsic viscosity were dilatant (i.e., viscosity increased with the increasing rate of shear). In cases where the thixotropy

or dilatancy was extremely marked, in *n*-butyl acetate, these characteristics tended to persist in the Hercules' solvent, acetone, and dibutyl phthalate. In cases of intermediate properties such as with sample N/C 2 at 5% concentration, the flow in Hercules' solvent was Newtonian, in *n*-butyl acetate slightly thixotropic, and in dibutyl phthalate very thixotropic.

It is also apparent from Table I, that the viscosities obtained at 1 to 5% concentrations followed generally, but not exactly, the trend of the intrinsic viscosities. Moreover, the variation from one solvent to another was considerable, especially in the case of the Hercules' solvent. Since this solvent will not dissolve fibers of high or low nitrogen content whereas both acetone and *n*-butyl acetate dissolve almost completely the nitrocelluloses investigated in this work, the differences in viscosity are not surprising.

In general, the viscosities were higher for equal concentrations in dibutyl phthalate and nitroglycerine (3), than in acetone or *n*-butyl acetate. The tendency towards thixotropy was in the same order; namely, acetone, *n*-butyl acetate, dibutyl phthalate, and nitroglycerine.

Table III shows the variation of properties with concentration for several nitrocelluloses. It is seen that with increase in concentration there was a definite tendency towards increased thixotropy. This was true whether the

TABLE III

VISCOSITY–RATE OF SHEAR VARIATIONS FOR CHANGING CONCENTRATION OF NITROCELLULOSE IN *n*-BUTYL ACETATE AT 20° C.

Nitrocellulose Reference No.	Concentration in *n*-butyl acetate, %	Viscosity in centipoises			
		10 r.p.m.	20 r.p.m.	30 r.p.m.	40 r.p.m.
19	2.00	2.78	3.78	4.33	4.41
	5.00	7.02	7.81	8.61	8.77
	8.00	20.7	22.0	22.4	22.4
	12.00	63.1	65.5	66.8	66.6
32	1.00	0.80	0.98	1.15	1.21
	2.00	2.65	3.11	3.62	3.71
	5.00	6.96	6.79	7.25	7.83
38	1.00	0.85	1.14	1.27	1.28
	5.00	83.0	83.5	83.6	81.2
2	1.00	19.1	21.3	22.3	21.8
	2.00	47.0	46.1	46.5	43.8
	5.00	1350	1340	1310	1255
	8.00	5940	5200	4920	4610
31	1.00	55.7	55.7	56.2	54.0
	5.00	1010	966	882	750
5	0.50	230	230	184	172
	1.00	1032	805	687	613
20	1.00	2.42	2.58	2.85	3.02
	5.00	1090	1108	1090	1058
39	1.00	4.39	4.85	5.29	4.75
	5.00	3530	3030	2780	2630

nitrocellulose solution was thixotropic or dilatant at low concentrations. If the solution was dilatant at low concentrations it passed through a shear-independent or Newtonian state before becoming thixotropic as the concentration increased. This is clearly shown in Fig. 1, where log $1/r.p.m.^2$ is plotted against viscosity.

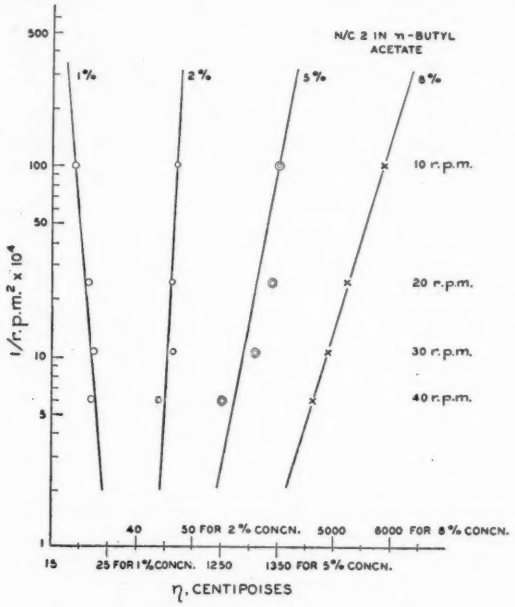


FIG. 1. *Change in rheology with concentration.*

In Table IV the effect of temperature on rheological properties is shown. In this case an increase in temperature decreased both the dilatant and thixotropic characteristics of the solutions and tended to make them less dependent on shear. This is shown graphically in Fig. 2.

In all the work recorded in this paper, care was taken to examine the viscosity–shear curves for 'hysteresis loops'. The readings were taken at equal times for each rate of shear, both with increasing steps and decreasing steps. The difference between them was in general found to be very small, viz., of the order of less than 2%, but, when the torque was applied over 30 min. a breakdown of about 10% of the initial reading was obtained with the most thixotropic solutions studied only if the original solution had been undisturbed for some time. The hysteresis loop in this case was appreciable, but the slope of both upward and downward portions was the same (Fig. 3). In Fig. 3 representative curves are given of the most thixotropic (N/C 5, 1%) and the most dilatant (N/C 19) solutions studied. In each case torque was applied at 40 r.p.m. for 30 min. (longer time gave no further change)

TABLE IV

RATE OF SHEAR–VISCOSITY CHANGES OF NITROCELLULOSE SOLUTIONS WITH TEMPERATURE

Nitrocellulose Reference No.	Temperature, °C	Concentration in *n*-butyl acetate, %	Viscosity in centipoises			
			10 r.p.m.	20 r.p.m.	30 r.p.m.	40 r.p.m.
19	20	12.0	63.1	65.5	66.8	66.6
	40	12.0	39.5	37.5	37.9	38.3
2	20	8.00	5940	5200	4920	4610
	40	8.00	4230	4090	4050	3930
5	20	0.50	230	203	184	172
	40	0.50	130	119.5	119.5	120.5

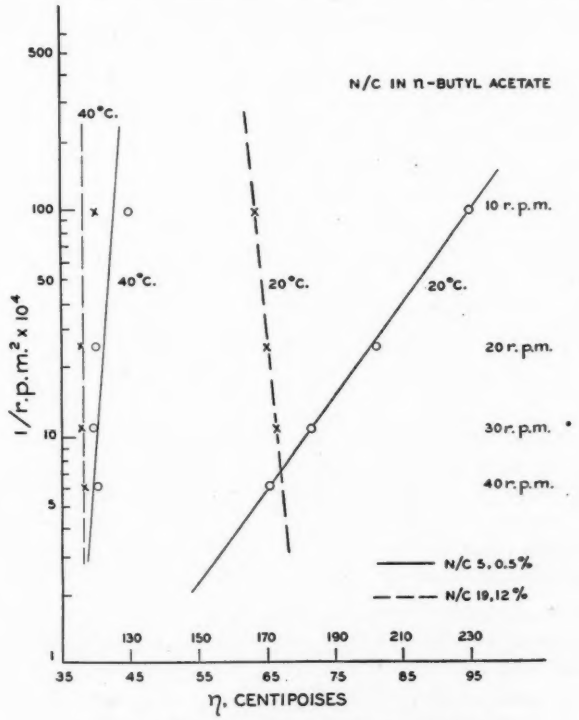


FIG. 2. *Change in rheology with temperature.*

before reducing the rate of shear. Hysteresis loops are apparent in both these curves. The descending arm was closely parallel to the ascending arm, which was different from the results obtained on printer's ink by Green and Weltmann (8). Our work, however, was done at much lower rates of shear.

On the whole, change in nitrogen content did not affect the rheological properties of nitrocellulose in acetone or *n*-butyl acetate to any marked extent. In both of these powerful solvents, the intrinsic viscosity, concentration, and temperature were the dominating conditions which determined

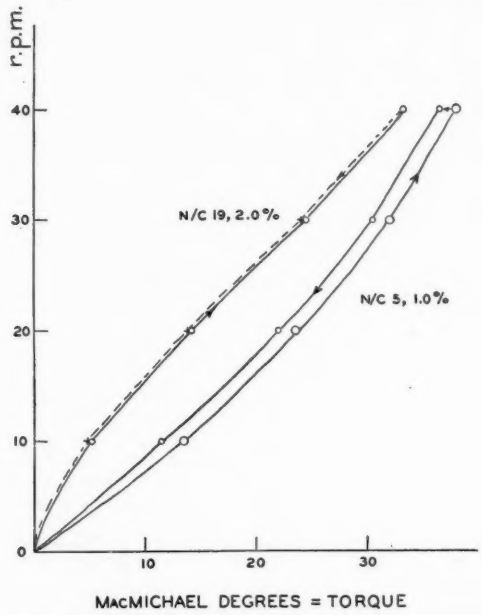


FIG. 3. *Anomalous viscosity loops. N/C in n-butyl acetate at 20° C.*

dilatancy or thixotropy. There was, however, a tendency for the viscosity to increase with the nitrogen content when intrinsic viscosity and concentration of solution remained the same. Thus, for nitrocelluloses of $[\eta]$ around 2.5, the viscosity of 5% solutions increased from 500 to 3000 centipoises as the nitrogen content rose from 10.6 to 13.4%. The tendency towards thixotropy, on the other hand, showed no consistent variation.

In this work, change of raw material and change of method of nitration did not show definite effects on the amount of thixotropy, although it is quite probable that the raw material may be important owing to the type and amount of impurity associated with it. Thus, unbleached linters or cops in every case gave both high viscosity and high thixotropy.

Discussion

The behavior of thixotropic solutions has been reviewed and discussed by Goodeve (1, 7). Goodeve considers that thixotropy arises when a scaffolding or network structure is present where particles interfere with one another

and form links. These links are broken and remade both by shear and by thermal movement, but the energy required to break the links must be of the order of kT*, otherwise the shear cannot concentrate sufficient force to break the link and it will be broken thermally. In shear-making the rate of collisions between particles capable of forming links is proportional to the rate of shear. Goodeve (7) has suggested that when a link breaks between two planes in the liquid, one moving and the other a reference plane, an impulse is given to the reference plane. Kauzmann and Eyring (9) have considered the subject of a network structure and they point out that, where links are being broken and reformed, an equilibrium is eventually reached where a constant retarding force is acting. However, the position of the equilibrium shifts with the rate of shear so that a falling-off of viscosity with increasing rate of shear is obtained. These authors also set up the equations for shear-making and shear-breaking, the latter being obtained by applying reaction rate theory to the problem, and considering how the potential function of the link is modified by the shearing force.

Using this model, the behavior of the nitrocellulose solutions can be explained satisfactorily. In dilute solutions, shear-making predominated over shear-breaking and dilatancy resulted. As the concentration increased, more links were present initially and shear-making became less important, until finally a state was reached where the effects were equal and the viscosity was independent of the rate of shear. If the concentration was further increased, shear-breaking predominated and the solutions became thixotropic. The effect of intrinsic viscosity was similar. The shorter the chain, the smaller the initial interference and therefore shear-making predominated. With larger chains, the initial interference was greater and shear-breaking became important. Goodeve (7) mentions the fact that suspensions of plate or rodlike particles are thixotropic down to concentrations as low as 1%. He also mentioned that upon aging, a treatment known to increase the length of the rods or the diameter of the plates, the suspensions became more thixotropic.

Similar results to those described in Table I were obtained by Rogowin and Iwanowa (14), who studied a series of nitrocelluloses of nitrogen content lying between 11.00 and 11.48% in ether–alcohol solutions (2 parts : 3). These authors evaluated structural viscosity by plotting the log of the velocity gradient against the viscosity in poises and using the slope of the line so obtained as a measure of structural viscosity, since a slope of zero corresponds to no structural viscosity. They found that most dilute solutions showed no structural viscosity but that solutions of higher concentrations did, the effect increasing rapidly with concentration. Structural viscosity increased with the specific viscosity of the samples but numerous exceptions were noticed. Philippoff (13) made a similar study on four nitrocelluloses in four different solvents and found that thixotropy varied with the type of solvent, being greatest in nitrobenzol and least in acetone. He also found that thixotropy decreased as the temperature rose. Previous studies on dilatant

* *k is Boltzmann's constant; T is the absolute temperature.*

solutions are also in accord with the trends shown in Table I. Daniel (2) observed that dilatancy was obtained with pigments if the attractive forces between particles were prevented from becoming dominant by the use of high potentials or other means. Gallay and Puddington (6) point out that correlation exists between dilatancy and sedimentation volume, dilatancy occurring in pastes, where the latter is small. All these observations support the view that shearing, by promoting collisions between particles, causes association and formation of structure in dilatant solutions.

Thixotropy has also been discussed by Green and Weltmann (8, 15). Their approach was more empirical than Goodeve's or Eyring's. From an analysis of a generalized consistency curve obtained with a rotating cylinder viscometer they predict a linear relation between plastic viscosity and the logarithm of the reciprocal of the square of the angular velocity. The fundamental assumption on which they base their analysis is that the loss in torque in going from zero to a given angular velocity is proportional to the rate of shear. This assumption is inherent in Eyring's picture, and Goodeve mentions that in cases where Brownian movement is high the number of links in the gel will decrease with increasing rates of shear. By a slight modification of the treatment of Green and Weltman for solutions that do not show a yield point, it can be shown that the apparent viscosity is approximately a linear function of the logarithm of the reciprocal of the square of the angular velocity. Some examples of these plots are shown in Figs. 1 and 2. It can also be shown that for dilatant solutions a similar relation holds. Examples of these latter plots are shown in Fig. 3; the slope of the line is called by Green and Weltman the coefficient of thixotropic breakdown, and it is a criterion similar to that of Rogowin and Iwanowa.

The effect of solvent has been discussed in a qualitative way by Huggins (10, Chaps. 1, 4, and 5). He points out that the coiling in solute chains will be tighter than that in purely random kinking if the average cohesive energy between like units, i.e., chain–chain or solvent–solvent, is greater than that between unlike units. This will result in a viscosity lower than the normal for a chain of given size. If, on the other hand, greater attraction between unlike units exists, the solute chain molecules will be more extended than in the case where kinking was purely at random and the viscosity for a given size of chain will be greater than in the random case. Recently Frith (5) has discussed the picture semiquantitatively and arrived at similar conclusions. She found, however, that the effect of temperature was to damp the effect of solvent, a fact that was not unexpected since increasing temperature will increase the molecular motions and tend to restore the inbiased viscosity. With this theory as a background, the behavior of such samples as N/C 12, 19, and 2 can be explained qualitatively. The change from dilatancy to thixotropy was accompanied by an increase in viscosity on changing N/C 12 from Hercules' solvent to *n*-butyl acetate, and hence an increase in effective chain length due to action of the solvent resulted. This increased effective chain length was enough to cause shear-breaking to predominate.

The effect of concentration has not been analyzed other than by the qualitative picture given above, since this was studied thoroughly only in a few cases in this work.

Acknowledgments

The authors are indebted to Dr. D. C. Rose and the Department of National Defence, Canada, for permission to publish this work. The assistance of Messrs. I.C.I. (Explosives) Ltd., Stevenston, Scotland, in submitting samples of nitrocotton for this investigation is also gratefully acknowledged.

References

1. ARNOLD, J. E. and GOODEVE, C. F. J. Phys. Chem. 44 : 652. 1940.
2. DANIEL, F. K. India Rubber World, 101 (4) : 33. 1940.
3. FENSOM, D. Can. J. Research, B, 24 : 83. 1946.
4. FREUNDLICH, H. and JONES, A. D. J. Phys. Chem. 40 : 1217. 1936.
5. FRITH, E. M. Trans. Faraday Soc. 41 : 17. 1945.
6. GALLAY, W. and PUDDINGTON, I. E. Can. J. Research, B, 21 : 179. 1943.
7. GOODEVE, C. F. Trans. Faraday Soc. 35 : 342. 1939.
8. GREEN, H. and WELTMANN, R. N. Ind. Eng. Chem., Anal. Ed. 15 : 201. 1943.
9. KAUZMANN, W. and EYRING, H. J. Am. Chem. Soc. 62 : 3113. 1940.
10. KRAEMER, E. O. Advances in colloid science. Vol. 2. Scientific progress in the field of rubber and synthetic elastomers. *Edited by* H. Mark and G. S. Whitby. Interscience Publishers, Inc., New York. 1946.
11. MEYER, K. H. High polymers, Vol. 4. Natural and synthetic high polymers; a textbook and reference book for chemists and biologists. *Translated by* L. E. R. Picken. Interscience Publishers, Inc., New York. 1942.
12. OTT, E. (editor) High polymers, Vol. 5. Cellulose and cellulose derivatives; a monograph prepared by a staff of specialists. Interscience Publishers, Inc., New York. 1943.
13. PHILIPPOFF, W. Z. angew. Chem. 49 : 855. 1936.
14. ROGOWIN, S. and IWANOWA, W. Kolloid-Z. 72 : 86. 1935.
15. WELTMANN, R. N. J. Applied Phys. 14 : 343. 1943.

UNE SYNTHESE DE LA *dl*-METHIONINE[1]

PAR ROGER GAUDRY ET GUY NADEAU

Résumé

La méthode de Livak pour la synthèse de la méthionine a été simplifiée en substituant à la 5-(β-bromoéthyl)-hydantoine, la 5-(β-chloroéthyl)-hydantoine qui est obtenue beaucoup plus facilement à partir de l'acétal β-chloropropionique et le rendement en méthionine a été porté à 35% à partir de l'acétal. D'autre part, la préparation de la 5-(β-méthylmercaptoéthyl)-hydantoine à partir de la β-méthylmercaptopropionaldéhyde obtenue par condensation directe de l'acroléine avec le méthyl mercaptan a permis d'obtenir la méthionine avec un rendement de 60% à partir de l'acroléine.

Introduction

Parmi les synthèses récentes de la méthionine, celle de Livak *et al.* (5), qui se fait à partir de la γ-butyrolactone par l'intermédiaire de la 5-(β-bromoéthyl)-hydantoine et de la 5-(β-méthylmercaptoéthyl)-hydantoine (VIII), nécessite de nombreuses étapes et le rendement total n'est pas très élevé.

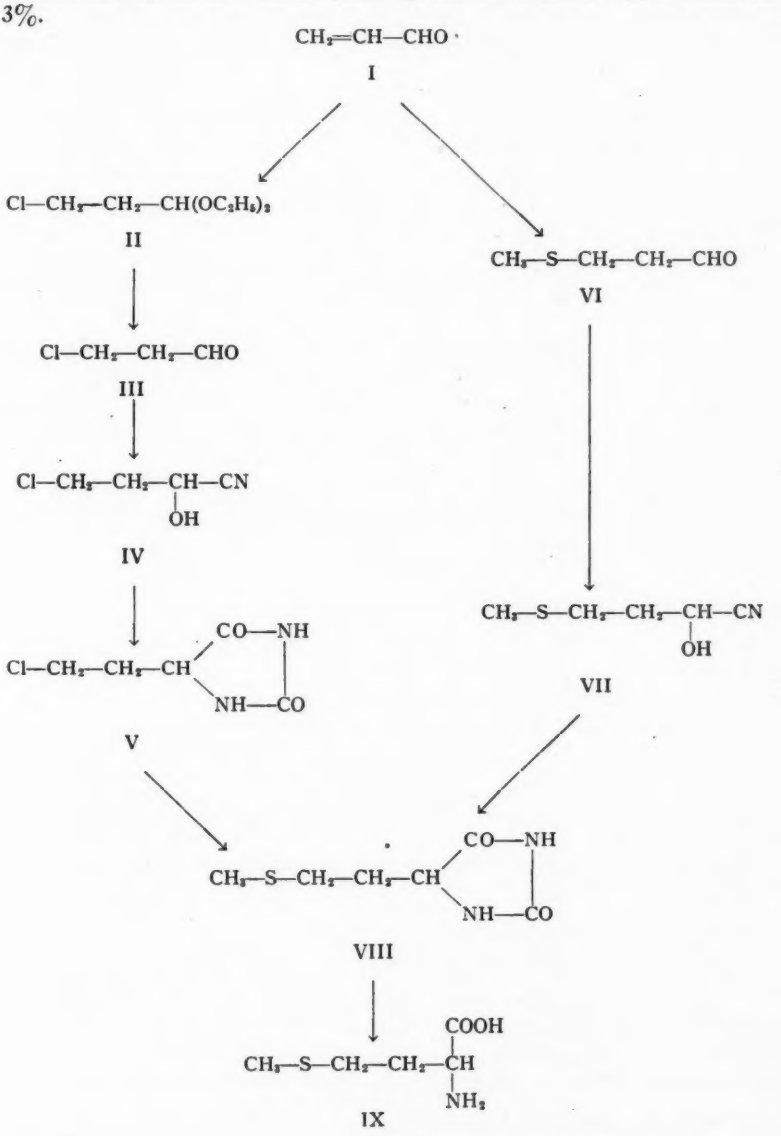
Nous avons pensé qu'il serait possible de simplifier cette méthode en substituant la 5-(β-chloroéthyl)-hydantoine (V) à la 5-(β-bromoéthyl)-hydantoine. Nous avons préparé cette hydantoine chlorée à partir de l'acétal β-chloropropionique (II) obtenu de l'acroléine (I) (6, pp. 137-138). Cet acétal est facilement hydrolysé en aldéhyde (III) correspondante par un acide minéral dilué. L'aldéhyde est alors transformée en cyanhydrine (IV) qui, traitée par le carbonate d'ammonium selon la méthode de Bucherer (2), donne la 5-(β-chloroéthyl)-hydantoine (V) avec un rendement de 50% à partir de l'acétal. Comme la réaction entre la cyanhydrine et le carbonate d'ammonium se fait en présence d'un excès de carbonate, il importe de ne pas élever la température au-dessus de 75° C. afin d'éviter la décomposition de la 5-(β-chloroéthyl)-hydantoine (V) qui est instable en milieu alcalin. La condensation de la 5-(β-chloroéthyl)-hydantoine (V) avec le méthyl mercaptate de soude pour donner la 5-(β-méthylmercaptoéthyl)-hydantoine (VIII) se fait tout aussi facilement qu'avec le dérivé bromé correspondant, avec un rendement de 75%. Le rendement total en méthionine (IX) est donc de 35% à partir de l'acétal β-chloropropionique (II) puisque l'hydrolyse finale de l'anneau de l'hydantoine au moyen de l'hydroxyde de baryum sous pression se fait avec un rendement de 95% (5).

Pour rémédier à l'instabilité relative de la 5-(β-chloroéthyl)-hydantoine (V), nous avons préparé la 5-(β-méthylmercaptoéthyl)-hydantoine (VIII) directement à partir de la β-méthylmercaptopropionaldéhyde (1, 3) que nous avons obtenue avec un rendement de 87%, en condensant l'acroléine (I) avec le méthyl mercaptan en présence d'une trace de triéthylamine. Nous avons

[1] *Manuscrit reçu le 27 novembre 1947.*

Contribution du Département de Biochimie de la Faculté de Médecine, Université Laval, Québec, Qué.

alors transformé l'aldéhyde en dérivé bisulfitique, puis en cyanhydrine correspondante (VII) et, par chauffage de la cyanhydrine avec un excès de carbonate d'ammonium (2), nous avons obtenu la 5-(β-méthylmercaptoéthyl)-hydantoine (VIII) avec un rendement de 73%, soit 63.5% à partir de l'acroléine (I). Le rendement total en méthionine (IX) à partir de l'acroléine (I) est donc de 60.3%.



Cette dernière méthode nous semble présenter de multiples avantages. Les rendements sont nettement supérieurs à ceux obtenus par Catch *et al.* (3) qui ont appliqué la méthode usuelle de Strecker. Les réactions se font en trois étapes seulement, les seuls produits intermédiaires qui ont été isolés à l'état pur étant l'aldéhyde et l'hydantoine. Enfin l'hydrolyse alcaline de l'hydantoine au moyen de l'hydroxyde de baryum permet d'obtenir directement l'acide aminé libre, sans qu'il soit nécessaire de passer par le chlorhydrate.

Partie Expérimentale

5-(β-Chloroéthyl)-hydantoine (*V*)

Un mélange de 16.4 g. d'acétal β-chloropropionique et de 100 ml. d'acide chlorohydrique normal fut agité et chauffé dans un bain-marie à 45° à 50° C. jusqu'à dissolution complète de l'acétal (environ 30 min.). A la solution refroidie, furent ajoutés 5 g. de cyanure de sodium, et le mélange fut agité pendant quatre heures à la température de la chambre. La cyanhydrine résultante fut extraite à l'éther et l'éther distillé dans un vide partiel. La cyanhydrine fut ajoutée à une solution de 19.2 g. de carbonate d'ammonium dans 50 ml. d'eau. Le mélange fut agité pendant une heure dans un bain-marie maintenu à 50° C. et l'excès de carbonate d'ammonium fut décomposé par distillation dans le vide en ayant soin de maintenir la température de la solution au-dessous de 75° C. La solution fut concentrée à petit volume et le résidu mis à la glacière. L'hydantoine cristallise lentement. Après traitement au noir animal, un produit blanc cristallin fut obtenu. Rendement: 8.2 g., 50%, P.f. 105° à 107° C.* Calculé pour $C_5H_7O_2N_2Cl$: N, 17.24%; Cl, 21.85%. Trouvé: N, 16.98%; Cl, 20.97%.

5-(β-Méthylmercaptoéthyl)-hydantoine (*VIII*)

A une solution de 1.15 g. de sodium métallique dans 50 ml. d'alcool absolu, refroidie dans un bain de glace et de sel, furent ajoutés lentement 2.5 g. de méthyl mercaptan préalablement refroidi, puis une solution de 8.1 g. de 5-(β-chloroéthyl)-hydantoine dans 75 ml. d'alcool absolu. Le mélange fut chauffé à reflux pendant une heure, la majeure partie de l'alcool évaporée et le résidu dilué avec de l'eau. La neutralisation avec de l'acide chlorhydrique 6 *N* donna un précipité cristallin blanc qui fut recristallisé de l'eau. Rendement: 6.5 g., 75%. P.f. 110° à 113° C. Litt.: 117° C. (4); 105° à 106° C. (5). Calculé pour $C_6H_{10}O_2N_2S$: N, 16.09%; S, 18.39%. Trouvé: N, 16.18%; S, 16.08%.

β-Méthylmercaptopropionaldéhyde (*VI*)

Dans un ballon de 100 ml. muni d'un long tube vertical, d'un entonnoir à décantation et d'un thermomètre plongeant au fond du récipient, furent placés 5 g. de méthyl mercaptan, préalablement refroidis au-dessous de 0° C., et une trace de triéthylamine. Le mélange fut refroidi à −40° C. en plongeant le ballon dans un bain d'alcool et de glace sèche et 5 g. d'acroléine furent ajoutés

* *Les points de fusion ne sont pas corrigés.*

goutte à goutte en maintenant la température au-dessous de 0° C. (A chaque addition d'acroléine, la température de mélange s'élève brusquement et il faut laisser le mélange se refroidir de nouveau avant d'ajouter l'acroléine, afin d'éviter la perte de méthyl mercaptan.) Une fois la réaction terminée, l'aldéhyde fut distillée dans le vide. P.é. 63° C. à 21 mm. Litt.: 60° C. à 12 mm. (1). Rendement: 8.1 g., 86.6%.

5-(β-Méthylmercaptoéthyl)-hydantoine (*VIII*)

A une solution agitée et refroidie de 6 g. de sulfite acide de sodium dans 15 ml. d'eau, furent ajoutés lentement 6 g. de β-méthylmercaptopropionaldéhyde, puis une solution de 3.8 g. de cyanure de potassium dans 15 ml. d'eau. Le mélange fut agité pendant une heure à la température de la chambre et la cyanhydrine résultante fut extraite à l'éther. L'éther fut distillé et la cyanhydrine ajoutée à une solution de 11.0 g. de carbonate d'ammonium dans 75 ml. d'alcool 50%. Le mélange fut agité pendant cinq heures dans un bain-marie maintenu à 55° C. et l'excès de carbonate d'ammonium fut décomposé par chauffage dans le vide. La solution fut concentrée à petit volume. L'hydantoine cristallise aussitôt. Rendement: 7.3 g., 73%. P.f. 104° à 106° C. Calculé pour $C_6H_{10}O_2N_2S$: N, 16.09%. Trouvé: 16.18%.

dl-Méthionine (*IX*)

Un mélange de 17.4 g. de 5-(β-méthylmercaptoéthyl)-hydantoine, de 50.5 g. d'hydroxyde de baryum octahydraté et de 300 ml. d'eau fut chauffé dans un autoclave à 160° C. pendant 30 min. et la *dl*-méthionine fut isolée suivant la méthode décrite par Livak (5). Rendement: 14.1 g., 95%.

Remerciements

Les auteurs remercient le Conseil National des Recherches pour l'octroi à l'un d'eux (G.N.) d'une bourse qui a permis la réalisation partielle de ce travail.

Bibliographie

1. Barger, G. et Coyne, F. P. Biochem. J. 22 : 1417. 1928.
2. Bucherer, H. T. et Lieb, V. A. J. prakt. Chem. 141 : 5. 1934.
3. Catch, J. R., Graham, A. R., Cook, A. H. et Heilbron, I. Nature, 159 : 578. 1947.
4. Hill, E. M. et Robson, W. Biochem. J. 30 : 248. 1936.
5. Livak, J. E., Britton, E. C., VanderWeele, J. C. et Murray, M. F. J. Am. Chem. Soc. 67 : 2218. 1945.
6. Witzemann, E. J., Evans, W. L., Hass, H. et Schroeder, E. F. *Dans* Organic syntheses, Collective Volume 2. Ed. par A. H. Blatt. John Wiley & Sons, New York et Chapman & Hall, Ltd., London. 1943.

THE EFFECT OF TEMPERATURE AND MIXED-SOLVENT COMPOSITION ON THE INTRINSIC VISCOSITY OF GR-S[1]

By L. H. Cragg and T. M. Rogers[2]

Abstract

The intrinsic viscosity of a sample of GR–S has been measured, at temperatures ranging from 0° to 65° C., in several solvents made progressively 'poorer' (to the point of precipitation) by the addition of nonsolvent. The results afford strong evidence in support of the theory (Flory; Alfrey, Bartovics, and Mark) that intrinsic viscosity is very sensitive to the shape assumed by a flexible long-chain molecule in solution and that this shape varies with the nature of the solvent and with the temperature. Measurements with various systems of the type GR–S–solvent–nonsolvent indicate that the intrinsic viscosity at the precipitation point is the same with different nonsolvents and, to a first approximation, with different solvents. This intrinsic viscosity is, moreover, independent of temperature.

Introduction

The intrinsic viscosity, $\lim_{c \to 0} \left(\frac{\eta_r - 1}{c} \right)$, is a function expressly designed to be independent of concentration and of the nature of the solvent (4) (for the contribution of the solvent to the relative viscosity of the solution is unity). Moreover, it should be relatively independent of temperature for although both η_s, the viscosity of the solution, and η_0, the viscosity of the solvent, vary greatly with the temperature, they vary to about the same degree so that the ratio η_s/η_0 (i.e., the relative viscosity η_r) is much more nearly independent of temperature (10). Nevertheless it is well known that in actual fact the intrinsic viscosity of a given polymeric substance is *not* necessarily the same in different solvents and that it may change considerably with changing temperature (9). This suggests that the shape assumed by the polymer molecules in solution, and therefore their contribution to the viscosity of the solution, must be dependent on the nature of the solvent and on the temperature of the solution.

In 1942, Alfrey, Bartovics, and Mark (2) advanced an hypothesis, based on an earlier suggestion of Flory (6), relating the shape assumed by a linear macromolecule in solution, and therefore the intrinsic viscosity of the polymeric substance, to the nature of the solvent. On the basis of this hypothesis they were able to explain why in some solvents an increase of temperature causes a decrease in $[\eta]$, in other solvents an increase, and they predicted (and in some rather qualitative experiments demonstrated) that when a

[1] *Manuscript received August 5, 1947.*

Contribution from the Department of Chemistry, McMaster University, Hamilton, Ont. From a thesis submitted in May, 1947, in partial fulfilment of the requirements for the degree of Master of Science. Presented at the 30th Canadian Chemical Conference, Banff, June, 1947.

[2] *Holder of a Bursary under the National Research Council of Canada, 1946–47. Present address: Research Laboratories, Imperial Oil Company Ltd., Sarnia, Ontario.*

polymer is 'precipitated' out of solution by the addition of a nonsolvent the intrinsic viscosity at the precipitation point is, to a first approximation at least, independent of the solvent *or* the nonsolvent. Although such an hypothesis should have stimulated a good deal of research, it has been strangely neglected, even by its authors (although Alfrey (1) has just recently discussed the theory in greater detail, and further evidence is being published (3)). It has, however, served as stimulus and guide for the investigation, here described, of the effect of temperature and solvent on the intrinsic viscosity of GR-S, an investigation which is part of a larger study of the variables affecting the evaluation of this important property of this important synthetic elastomer.

The theory of Alfrey, Bartovics, and Mark may be summarized, in their own words, as follows:

"A long chain hydrocarbon molecule in solution takes on a somewhat kinked or curled shape, intermediate between a tightly rolled up mass and the rigid linear configuration assumed by Staudinger. Presumably all possible degrees of curling are represented, owing to the internal Brownian movement of the flexible chains, but the configurations of intermediate extension predominate statistically. The average or effective value of any shape-dependent molecular property (such as hydrodynamical influences) may be obtained by summing this property over all configurational states, after each state has been given a proper weight factor. If the long chain molecule is surrounded by a continuous, energetically indifferent solvent, then the weight factor for a particular configuration is determined only by internal parameters —potential energy function for restricted rotation, prohibition of segment interpenetration, etc. The mean value of any molecular property in such an indifferent (and perhaps hypothetical) solvent might be called the 'unbiased' statistical mean for the property.

"If the solvent is energetically unfavorable, so that the dissolving of the high polymer is an endothermic process, then the polymer segments will attract each other in solution and squeeze out the solvent between them. . . . Those molecular configurations which involve many contacts of the molecule with itself will be weighted more heavily than in an indifferent solvent, and the mean value of any molecular property will represent a more curled and contracted shape than the unbiased mean. On the other hand, if a solvent is energetically more favorable than the indifferent solvent as previously defined, then in solution the long chain molecule will be surrounded by a solvated hull which tends to prevent polymer-polymer contacts. Uncurled configurations will be favored, and the mean value of any property will represent a more extended shape than the unbiased mean. Since an extended or uncurled configuration is associated with a high intrinsic viscosity, and *vice versa*, the first prediction as to effect of solvent type upon viscosity is the following: Other conditions being equal, a given high polymeric material made up of flexible molecules will exhibit a high intrinsic viscosity in an energetically favorable solvent, and a low intrinsic viscosity in an energetically unfavorable solvent . . . If a good solvent is mixed with a precipitating agent, the resulting mixture

can be expected to be energetically less favorable to a long chain molecule than is the pure solvent. A dilute solution of high polymer in a solvent-nonsolvent mixture should, therefore, exhibit a lower intrinsic viscosity than a solution of the same polymer in the pure solvent. . . . . .

"The effect of temperature upon intrinsic viscosity should depend strongly upon the nature of the solvent. In a poor solvent, the effective molecular shape is more compact and curled than the unbiased statistical mean. An increase of temperature should increase the relative importance of entropy factors over energetic factors and result in an uncurling of the molecule. In such a solvent, a temperature increase should result in an increase of intrinsic viscosity. In a very good solvent, the energetic weighting factors favor the more extended configurations; here a temperature increase should result in a downward approach to the unbiased statistical mean shape. In a very good solvent, therefore, a temperature increase should cause a decrease in intrinsic viscosity. There should be an intermediate case in which the intrinsic viscosity is independent of temperature over a limited range. . . . . .

"We have interpreted variations in the intrinsic viscosity of a given high polymeric material as being due to changes in the degree of *intramolecular* agglomeration. If this interpretation is correct, there should be also a close connection between the intrinsic viscosity of a high polymer solution and the degree of *intermolecular* agglomeration. Exactly the same solvent characteristics which determine the mean geometrical properties of an isolated long chain molecule should also determine the amount of association of different solute molecules into aggregates. When a non-solvent is added to a high polymer solution, the point at which precipitation begins represents a certain definite agglomeration tendency for chain segments of different molecules. To a first approximation, therefore, it should represent a certain definite mean value for any shape-dependent *internal* property. That solvent composition which is critical from the standpoint of solubility should correspond to a certain intrinsic viscosity, no matter what the solvent and what the non-solvent. One would therefore conclude the following: The intrinsic viscosities of a series of solutions of a given polymer in solvent–non-solvent mixtures of increasing non-solvent content, should decrease to a final value at the limit of solubility. This final value should be in first approximation the same in all solvent–non-solvent systems."

Alfrey (1) has recently pointed out that one should expect marked differences in sensitivity to solvent composition between polymeric substances with flexible molecules and those, like cellulose acetate (12) for example, whose molecules are relatively rigid. The effects of changes in temperature and of differences in the solvent should be most pronounced, and best in accord with the theory, when the polymer molecules "(a) are fairly uniform in their structure (specifically, do not have groups distributed along the chain which are much more polar than the bulk of the chain) and (b) are fairly flexible in solution."

It is reasonable, therefore, to test the validity of the theory by observations on systems, of the type polymer–solvent–nonsolvent, in which GR–S is the polymer. In this investigation three different solvents were used: benzene, xylene, and carbon tetrachloride. Benzene was chosen because it is the solvent most frequently used with GR–S both for intrinsic viscosity measurements and in fractionation studies. It can be classed as an 'indifferent' solvent for GR–S, for in benzene the intrinsic viscosity of GR–S is independent of temperature (10). Carbon tetrachloride and xylene were chosen to represent 'good' solvents; one of them is in many respects similar to benzene, the other is quite unlike it. Over a range of temperatures each of these solvents was made progressively poorer by the addition of a nonsolvent such as methanol and the resulting mixed-solvents used for determining intrinsic viscosities. Particular attention was paid to the determination of the intrinsic viscosity at the precipitation point, i.e., at that composition of mixed-solvent such that any further addition of nonsolvent would cause precipitation of polymer.

Experimental Work

Apparatus and Materials

The viscometric apparatus and technique have already been reported in detail (5), including the constants of the viscometer (10). Temperatures were regulated, as before, to $\pm 0.02°$ C., (except that for convenience a 'Magnaset' thermoregulator (Emil Greiner, N.Y.) replaced the Dekhotinsky type used in the earlier work). For measurements at 0° C. an ice–water mixture at equilibrium was used, giving a temperature of $0.03° \pm 0.03°$ C.

The *polymer*, normal plant GR–S, was obtained from Polymer Corporation, Ltd., Sarnia, on July 9, 1946. The analysis supplied with it was as follows:

CHEMICAL ANALYSIS — POLYMER NO. 2358

Constituent	%
Ash	0.79
Sol. ash	0.61
Free soap	0.20
Free fatty acid	5.07
*E.T.A.	7.65
Bound styrene	23.2
B.L.E. (antioxidant)	1.95

* *Portion soluble in ethanol–toluene azeotrope.*

The polymer remained gel free throughout the period of experimentation and its intrinsic viscosity in benzene at 25° C. did not change. In all experiments, the polymer was used as received, i.e., without preliminary extraction or fractionation.

Solvents (using the word in such a wide sense that it includes the nonsolvents)

Benzene—(Steel Co. of Canada) freed from thiophene by the method of Holmes and Beeman (7) and redistilled; B. range 79° to 80° C.

Xylene—(Steel Co. of Canada) commercial 10°, dried over calcium oxide, redistilled; B. range 136° to 136.5° C.

Carbon tetrachloride—(Nicholls Chemical Co.), dried over calcium chloride, redistilled; B. range 76° to 76.5° C.

Methanol—(Carbide and Carbon Chemical Corp.), dried over calcium oxide, redistilled; b.p. 63.7° C.

Ethanol—(Gooderham and Worts), dried over calcium oxide, redistilled; B. range 78° to 78.4° C.

2-Propanol—(Eastman Kodak) reagent grade.

1-Butanol—(Eastman Kodak) reagent grade.

Acetone—(Mallinckrodt), dried over calcium oxide, redistilled; B. range 56° to 56.5° C.

Benzyl alcohol—(Eastman Kodak) reagent grade.

Experimental Procedure

The solutions in each case were prepared by weighing out into dry 100 ml. volumetric flasks the appropriate amount of polymer, previously cut into cubes about 1 mm. to the side, and adding approximately 60 ml. of solvent, after which dissolution was allowed to take place in the dark. The amount of solvent added was adjusted so that sufficient space was left in the flask for the addition of nonsolvent. A period of 24 hr. was sufficient for complete dissolution. The solutions were then brought up to the temperature at which the flow time was to be determined, and were made up to volume by the addition of solvent of the same temperature. When mixed-solvents were used, the nonsolvent was added *after* the dissolution of the polymer in the pure solvent. The nonsolvent was added slowly from a burette at room temperature, and then the solution was made up to volume at the temperature of the experiment by the addition of more solvent. The necessary volume correction was applied in each case to determine the volume of the nonsolvent at the temperature of the experiment. The contents of the flask was constantly agitated during the addition of nonsolvent in order to prevent local excess of nonsolvent, which in most cases caused the formation of a coagulum which was difficult to redissolve.

The precipitation point was taken as the point at which the first permanent translucency appeared on addition of nonsolvent, the solution being viewed against a dark background under constant illumination. It could be located precisely*, but careful technique was necessary in order to bring the total volume of the solution at the end point to 100 ml. A rough determination of the amount of nonsolvent required was made, and then the end point

* *By holding a printed sheet behind the flask and noting the point at which the print lost sharpness of outline and became fuzzy and indistinct.*

obtained accurately by adding alternately solvent and nonsolvent until the volume was 100 ml.; at this point one drop of solvent would dissolve the precipitate formed, and one drop of nonsolvent cause precipitation again.

Before measurements of flow time were made, both the viscometer and the solution (or solvent) were suspended in the bath till thermal equilibrium was attained. The contents of the flask was thoroughly mixed by gently inverting the flask several times; 10 ml. of the liquid was then measured into the viscometer and the flow time determined. Check determinations were run in each case. After the run, the viscometer was cleaned by flushing with solvent, and dried. Flow times of pure solvent were redetermined at intervals to ensure constancy of conditions and technique.

Experimental Results

System GR-S—Benzene—Methanol

The intrinsic viscosity of GR-S in various mixtures of benzene and methanol was determined, by the one-point method (5) as $8\left(\frac{\nu_r^{1/8}-1}{c}\right)^{\dagger}$, at temperatures ranging from 10° to 50° C. Below 10° C. the solution is very viscous (f.p. of benzene is 5.5° C.); above 50° C. the methanol evaporates at an appreciable rate. The results are given in detail in Table I, and are shown graphically in

TABLE I

VARIATION OF INTRINSIC VISCOSITY WITH MIXED-SOLVENT COMPOSITION FOR SYSTEM GR-S–BENZENE–METHANOL

(c = 0.2500 gm. GR-S per 100 ml. solution)

Temp., °C.	Vol. % methanol	t_s, sec., ± 0.1	t_0, sec., ± 0.1	$[\eta]$
10	0	342.8	210.0	2.06
		342.9	210.0	
		342.9		
	4.0	319.4	204.7	1.86
		319.4	204.6	
	8.0	303.1	202.1	1.69
		303.2	202.2	
	12.0	284.2	202.7	1.41
		284.2	202.7	
	15.0	265.6	203.5	1.11
		265.7	203.6	
	*17.3	249.5	205.8	0.80
		249.5	205.8	
25	0	278.2	170.3	2.07
		278.4	170.3	
	4.0	259.3	164.5	1.91
		259.3	164.5	
	8.0	247.8	163.5	1.75
		247.8	163.6	

* *These are the precipitation points; the corresponding values of* $[\eta]$ *are designated in the text* $[\eta]_{prec.}$

† *It should be emphasized that all values of intrinsic viscosity reported in this paper were calculated as intrinsic kinematic viscosity* $[\nu]$, *using the calibration constants of the viscometer. The difference between* $[\nu]$ *and* $[\eta]$ *is assumed to be negligible (see (10)).*

TABLE I—*Concluded*

VARIATION OF INTRINSIC VISCOSITY WITH MIXED SOLVENT COMPOSITION FOR SYSTEM GR-S-BENZENE-METHANOL—*Concluded*

(c = 0.2500 gm. GR-S per 100 ml. solution)

Temp., °C.	Vol. % methanol	t_s, sec., ± 0.1	t_0, sec., ± 0.1	$[\eta]$
	12.0	233.6	163.3	1.50
	15.0	222.6	164.0	1.28
		222.4	164.0	
	*19.1	200.6	164.7	0.82
35	0	246.1	150.9	2.07
		246.1	150.9	
	4.0	230.5	146.0	1.94
		230.5	146.0	
	8.0	220.5	145.2	1.77
		220.6	145.2	
	12.0	208.6	144.0	1.57
		208.6	144.0	
	15.0	199.7	144.0	1.38
		199.8	144.1	
	*20.2	178.7	144.7	0.80
		178.5	144.6	
45	15.0	184.2	131.2	1.45
		184.3	131.2	
	*21.4	160.5	131.4	0.84
		160.6	131.4	
50	0	209.0	128.7	2.07
		209.1	128.7	
	4.0	201.7	126.8	1.98
		201.7	126.9	
	8.0	193.8	125.7	1.85
		193.7	125.6	
	12.0	186.2	126.1	1.66
		186.1	126.1	

* *These are the precipitation points; the corresponding values of* $[\eta]$ *are designated in the text* $[\eta]_{prec.}$

various ways in Figs. 1, 2, and 3. That the intrinsic viscosity may safely be determined by the one-point method even in the mixed-solvents is evident from the data of Fig. 4.

In Table I each value of t_s or t_0 represents the mean of at least two closely agreeing values; the duplicate values at a given concentration are those obtained in separate titrations. These figures therefore give a good indication of the precision of the experiments. In general, intrinsic viscosities obtained with all the systems investigated were precise to ± 0.02 or better, except at the precipitation points, where however the precision in multiplicate determinations was still ± 0.03 unit.

System GR-S—Benzene—Nonsolvent

The precipitation curves, obtained at 25.0° C., using four different nonsolvents, methanol, ethanol, 2-propanol, and acetone, are compared in Fig. 5. The lowest point on each curve is the precipitation point.

System GR-S—Carbon Tetrachloride—Methanol

Measurements were made at temperatures ranging from 0° to 45° C. The results are shown graphically in Figs. 7, 8, and 9. The validity of the one-point method of determining $[\eta]$ is attested by the plots in Fig. 6 as well as by the more complete data of Mr. K. Lounsbury (8) (who also proved the method satisfactory over the whole temperature range).

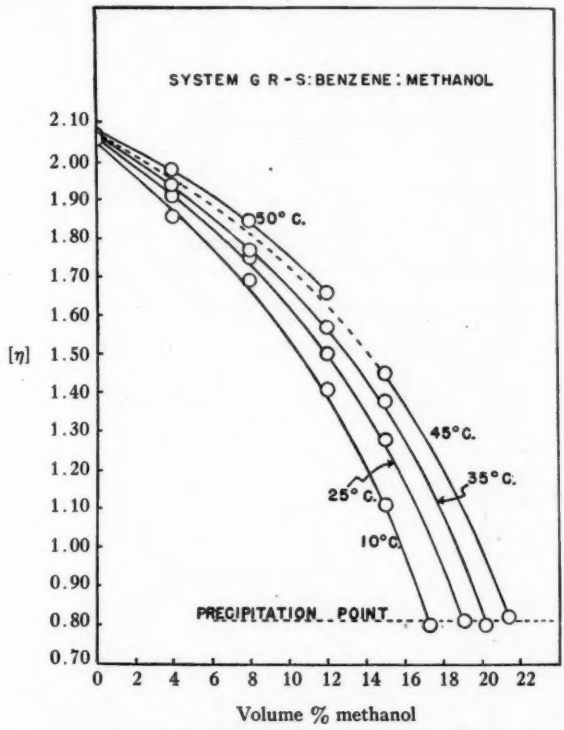


FIG. 1. *Variation of $[\eta]$ with composition of mixed solvent: benzene–methanol.*

System GR-S–Xylene–Methanol

Data were obtained over the temperature range 0° to 50° C. (and at 65° C. with pure xylene). They are presented graphically in Figs. 10, 11, and 12. Again the one-point method was shown to be valid for these experiments.

System GR-S—Solvent—Nonsolvent

Values of $[\eta]$ at the precipitation point were obtained with 12 different solvent–nonsolvent pairs. They are assembled for purposes of comparison in Table II.

TABLE II

VALUE OF $[\eta]$ AT PRECIPITATION POINT FOR SYSTEM GR–S–SOLVENT–NONSOLVENT

Temp. 25° C.
c = 0.2500 gm. GR–S per 100 ml. solution

Solvent	Nonsolvent	Vol. % nonsolvent	t_s, sec., ±0.1	t_0, sec., ±0.1	$[\eta]_{prec}$	Average
Benzene	Methanol	19.1	200.6	164.7	0.82	
"	Ethanol	24.2	218.3	180.0	0.80	0.81 ± 0.01
"	2-Propanol	36.3	241.3	198.8	0.80	
"	Acetone	49.6	147.3	121.9	0.80	
CCl_4	Methanol	17.5	184.5	145.4	0.99	
"	Ethanol	22.3	203.0	161.0	0.95	0.97 ± 0.02
"	1-Butanol	38.2	276.0	219.0	0.96	
"	Acetone	58.0	127.8	101.8	0.95	
Xylene	Methanol	17.5	223.6	175.5	0.99	
"	Ethanol	21.5	247.3	193.3	1.01	0.99 ± 0.02
"	1-Butanol	35.6	312.5	246.6	0.97	
"	Acetone	50.3	157.5	125.3	0.97	

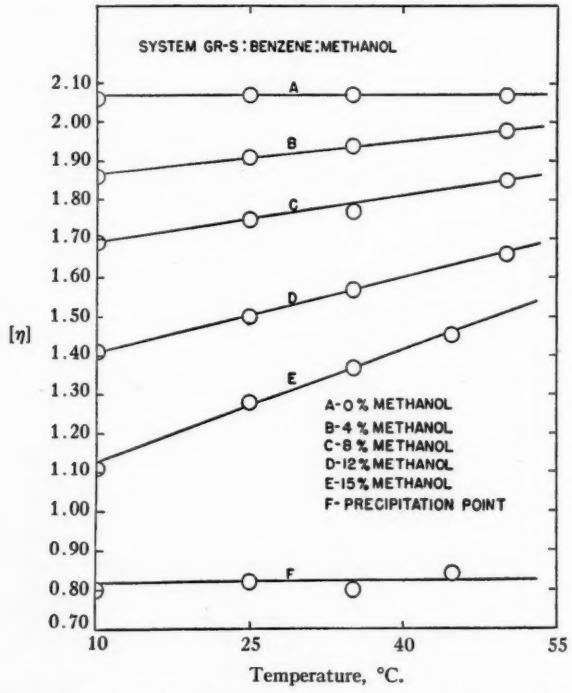


FIG. 2. *Variation of* $[\eta]$ *with temperature, in mixed solvents; variation of* $[\eta]_{prec}$ *with temperature, in mixed solvents.*

Discussion

It is evident at once that these results afford striking confirmation of the predictions of Alfrey, Bartovics, and Mark and, therefore, strong support for their theory. As the evidence is more detailed and more precise than that hitherto available, it is perhaps worth examining more fully.

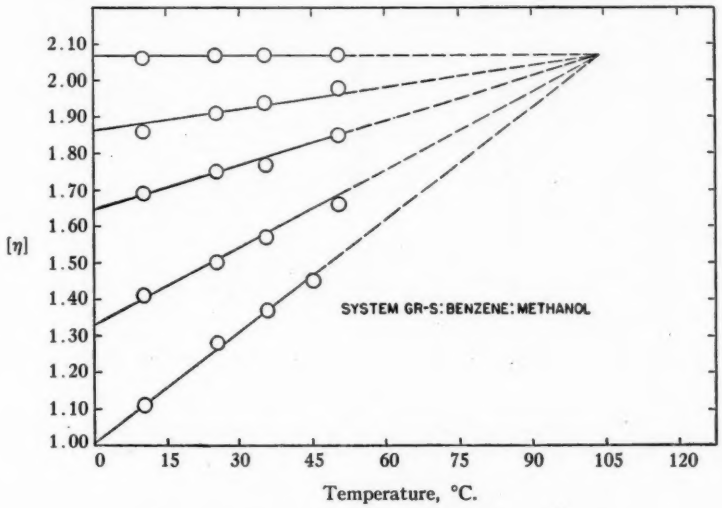


FIG. 3. *Lines of Fig. 2 extrapolated to higher temperatures.*

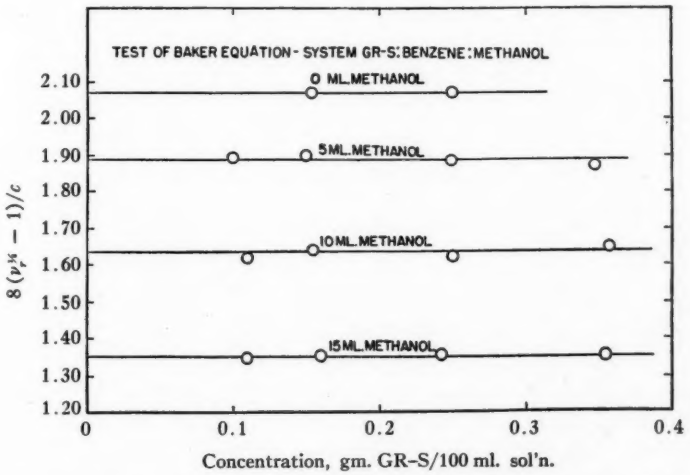


FIG. 4. *Test of the modified Baker equation ($n = 8$) for the system GR-S–benzene–methanol.*

Solvent Effects

"Polymer in a solvent–non-solvent mixture should . . . exhibit a lower intrinsic viscosity than . . . in the pure solvent." It is obvious from Figs. 1, 5, 7, and 10 that this prediction is abundantly fulfilled. As nonsolvent is added the

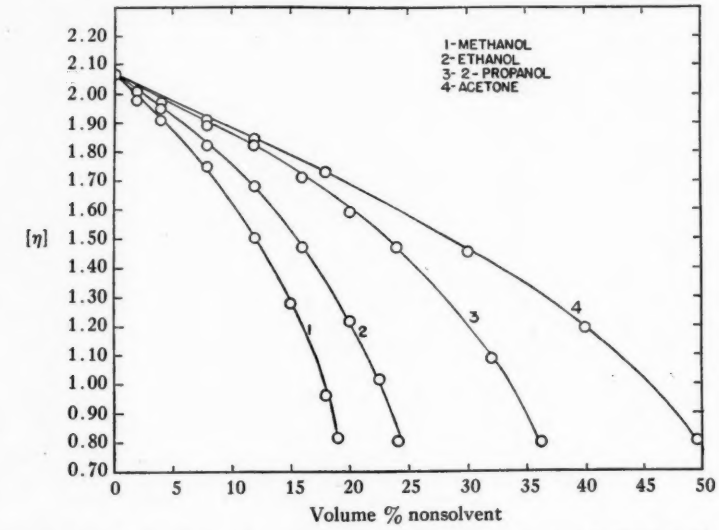


FIG. 5. *Effect of different precipitants on the intrinsic viscosity of GR–S in the mixed solvent: benzene–precipitant.*

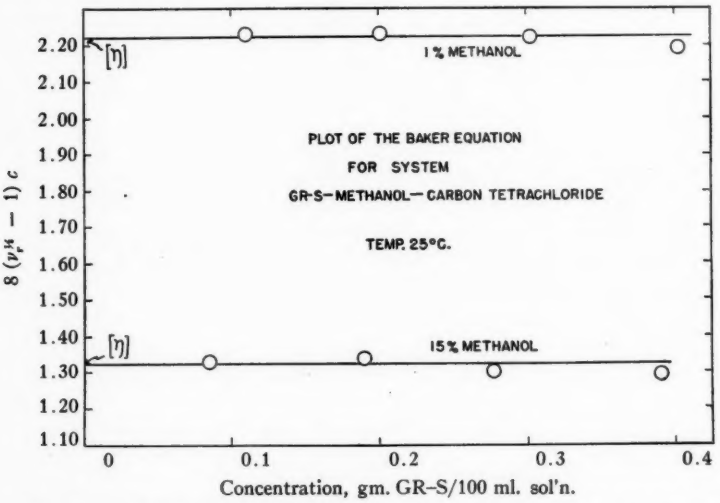


FIG. 6. *Test of the modified Baker equation (n = 8) for the system GR–S–carbon tetrachloride–methanol.*

intrinsic viscosity drops progressively until the solvent mixture becomes so 'poor' a solvent that the highest molecular weight species begins to settle out. It is interesting to note that when a sample of GR–S from the same bale was fractionated by precipitation with methanol from solution in benzene the intrinsic viscosity of the solution after the first (small) fraction was precipitated was found to be 0.82 (11), the value of $[\eta]_{prec}$ found in this investigation.

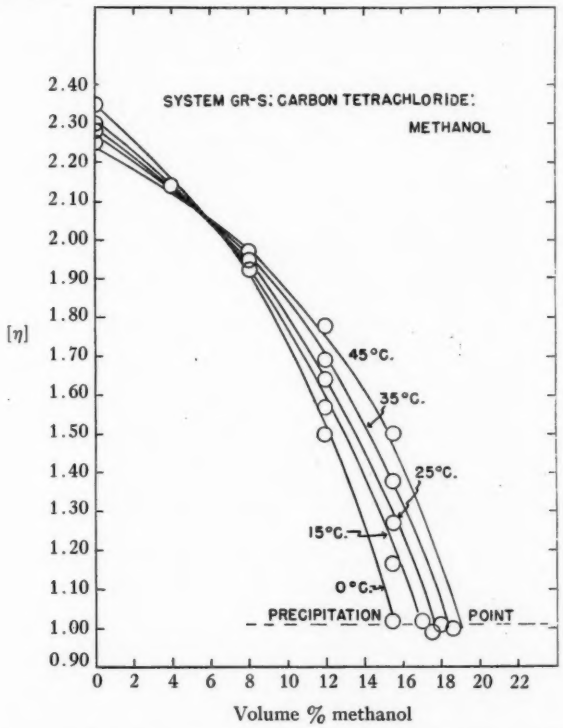


FIG. 7. *Variation of* $[\eta]$ *with composition of mixed solvent: carbon tetrachloride–methanol.*

Temperature Effects

"In a poor solvent . . . a temperature increase should result in an increase of intrinsic viscosity . . . In a very good solvent . . . a temperature increase should cause a decrease in intrinsic viscosity. There should be an intermediate case in which the intrinsic viscosity is independent of temperature over a limited range."

Again the predictions are borne out. Benzene is itself "an intermediate case" for when it is the solvent $[\eta]$ is independent of temperature (Fig. 2; *cf.* ref (2)). If it is made a 'poorer' solvent by the addition of any one of

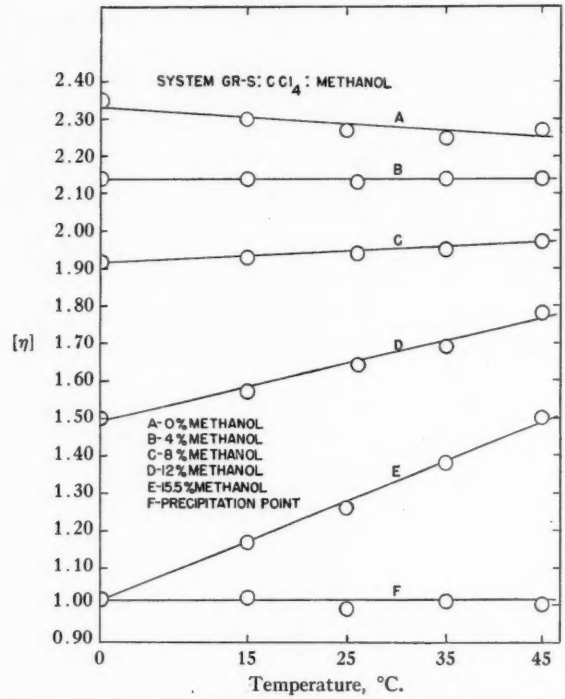


FIG. 8. *Variation of* $[\eta]$ *with temperature in mixed solvents; variation of* $[\eta]_{prec}$ *with temperature.*

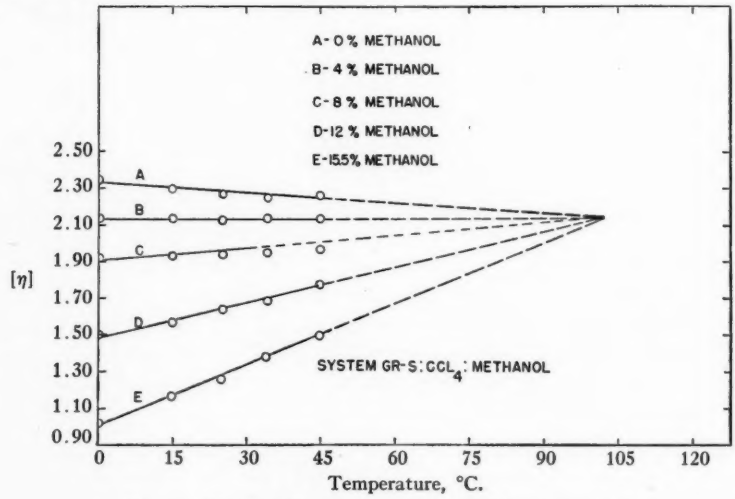


FIG. 9. *Lines of Fig. 8 extrapolated to higher temperatures.*

several nonsolvents, an increase of temperature causes an increase in $[\eta]$, and the slope $\frac{\Delta[\eta]}{\Delta\theta}$ becomes increasingly greater as nonsolvent is progressively added.

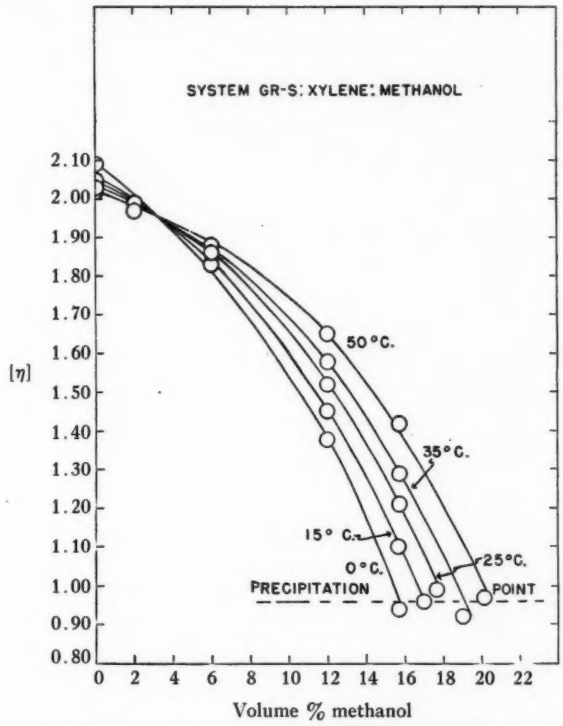


FIG. 10. *Variation of* $[\eta]$ *with composition of mixed solvent: xylene–methanol.*

Carbon tetrachloride and xylene are better solvents than benzene in the sense that a temperature increase results in a decrease in intrinsic viscosity. (It should be pointed out, however, that although at 25° C. $[\eta]$ is, as expected, larger in carbon tetrachloride than in benzene, it is somewhat *smaller* in xylene than in benzene. This is an instance, apparently, of "other things *not* being equal".) With carbon tetrachloride the "energetically indifferent solvent" medium is attained when methanol has been added to the extent of 4% by volume (Fig. 8). With xylene a slightly greater proportion of methanol is required (Fig. 11).

Plotting the results as in Figs. 2, 8, and 11 has several advantages over the usual method. For one thing the changes with temperature are much more clearly displayed; for another, the existence of an "energetically indifferent solvent" is emphasized and an excellent means of determining its composition

(by interpolation) provided. It becomes clear immediately that the effect of increasing the temperature is to make the solute molecules, in no matter what solvent–nonsolvent mixture, behave more and more as they do in the

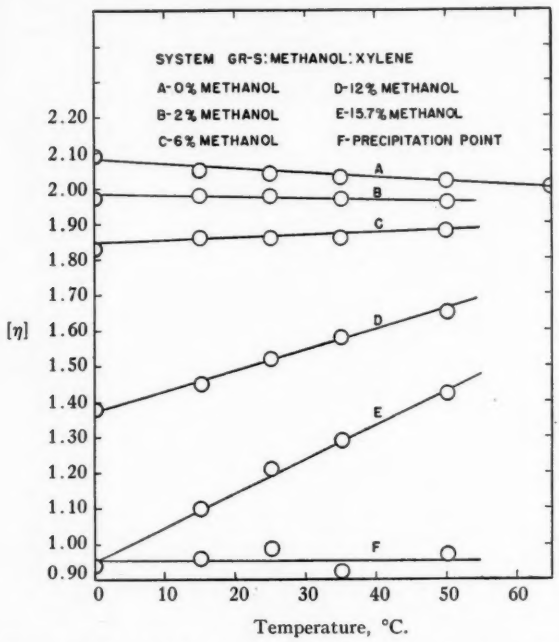


FIG. 11. *Variation of* $[\eta]$ *with temperature in mixed solvents; variation of* $[\eta]_{prec}$ *with temperature in mixed solvents.*

indifferent solvent. According to the theory, the increased Brownian movement of the long-chain molecules results in their assuming configurations which, on the average, approach more and more to the "unbiased statistical mean" configuration. Finally, when the straight lines in these figures are produced to higher temperatures a rather astonishing thing happens: the lines meet *at a common point.* This is true of all three systems investigated (Figs. 3, 9, and 12)! This suggests that if the temperature were made high enough the differences in the various solvent mixtures would disappear, and the polymer molecules would behave in each one of them as if it were the indifferent solvent. Moreover, the temperature of intersection is the same (within the error of extrapolation) for all three systems, namely, about 103° C. This remarkable agreement must surely have some significance; it suggests that this temperature might be a property of the only common constituent of these systems, the polymer.

It may be of course that the lines do not in reality remain straight at the higher temperatures but approach each other asymptotically; indeed it seems

much more natural to suppose, in the absence of data, that the lines would gradually merge rather than intersect sharply with a resulting discontinuity. Obviously the point cannot be settled experimentally with these systems,

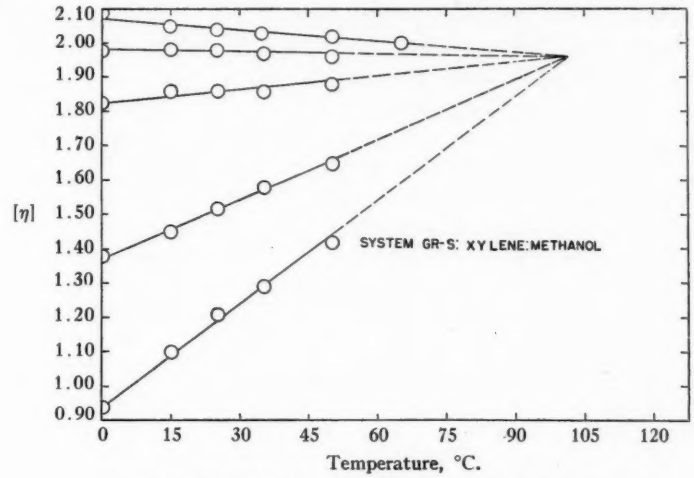


FIG. 12. *Lines of Fig. 11 extrapolated to higher temperatures.*

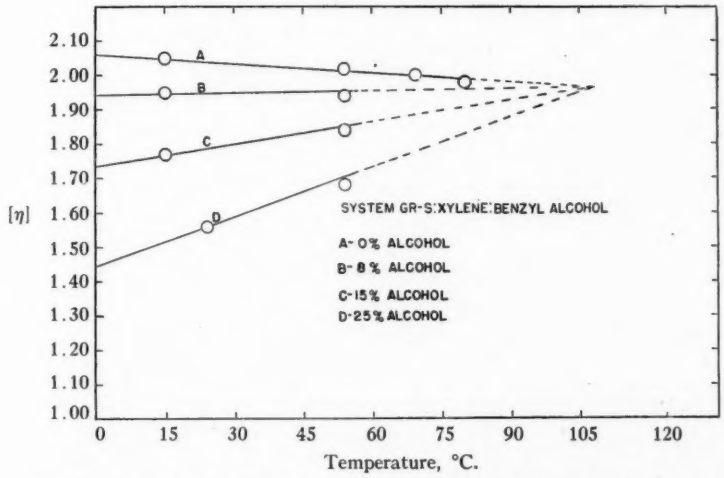


FIG. 13. *Variation of* [η] *with temperature, in mixed solvents: xylene–benzyl alcohol.*

but further investigation is underway with systems such that temperatures above 100° C. can be realized. Preliminary results with one such system: GR–S–xylene–benzyl alcohol, are shown in Fig. 13. As indicated, it is possible to persuade the lines to converge at about 105° C. but the crucial

high-temperature points are not yet available. (The difficulty is not entirely that of making measurements at elevated temperatures. We have some evidence that for this system, unlike the others, the one-point method for determining $[\eta]$ cannot safely be used, for the slope of the $8\left(\frac{\nu_r^{1/8}-1}{c}\right)$ vs. c curve deviates more and more from zero as the proportion of nonsolvent in the solvent–nonsolvent mixture increases (8).)

Intrinsic Viscosity at the Precipitation Point

The theory predicts that $[\eta]_{prec}$ "should be in first approximation the same in all solvent–non-solvent systems". The evidence in support of this prediction in the original paper was scanty and inconclusive; that recently published (1) is much more satisfying, though still based largely on results apparently obtained by rather lengthy extrapolation of "precipitation curves". The results reported here (Table II) are convincing proof of the correctness of the predictions as applied to GR–S systems, for in every instance $[\eta]_{prec}$ was measured directly, and with great care.

The intrinsic viscosity at the precipitation point is shown to be independent of the nonsolvent: with benzene four different nonsolvents of widely different precipitating power give values all in the range 0.81 ± 0.01; with carbon tetrachloride four different values of $[\eta]_{prec}$ lie in the range 0.97 ± 0.02, with xylene, in the range 0.99 ± 0.02. Even when the solvent is changed, $[\eta]_{prec}$ still remains approximately the same. With all the solvent–nonsolvent pairs studied the values of $[\eta]_{prec}$ fall in the range 0.9 ± 0.1.

It follows from the hypothesis, also, that the intrinsic viscosity at the precipitation point should be independent of the temperature at which precipitation is effected. That such is indeed the case with GR–S is evident from Figs. 2, 8, and 11 (the points at the bottom of each) and from the data in Table III. Since these observations were made, Alfrey (1) has published other convincing proof that $[\eta]_{prec}$ is independent of temperature; in his experiments the polymer was fractionated polystyrene.

TABLE III

VARIATION OF $[\eta]_{prec}$ WITH TEMPERATURE

System GR–S–solvent–methanol

Temperature °C.	Solvent					
	Benzene		Carbon tetrachloride		Xylene	
	% methanol	$[\eta]_{prec}$	% methanol	$[\eta]_{prec}$	% methanol	$[\eta]_{prec}$
0			15.5	1.02	15.7	0.94
10	17.3	0.80				
15			17.0	1.02	16.5	0.96
25	19.1	0.82	17.5	0.99	17.5	0.99
35	20.2	0.80	18.0	1.01	19.0	0.92
45	21.4	0.84	18.6	1.00		
50					20.1	0.97

It seems to be well established, therefore, that when a flexible polymer of relatively simple structure, such as GR–S or polystyrene, is dissolved in a solvent, and nonsolvent gradually added to the solution, the intrinsic viscosity of the polymer decreases until, at the point of precipitation, it has a value characteristic of the particular polymer used but almost independent of the temperature and of the nature of the solvent and nonsolvent.

This investigation has been carried out with unfractionated GR–S. It will be interesting to continue it, using fractionated samples of high and low molecular weight; one would expect that much greater effects would be observed with very long molecules than with short ones. Also, GR–S, being a copolymer, is not as simple in structure as the related polymers, polystyrene and polybutadiene. Alfrey has investigated polystyrene; polybutadiene remains to be studied and should prove equally interesting.

References

1. ALFREY, T., JR. J. Colloid Sci. 2 : 99. 1947.
2. ALFREY, T., JR., BARTOVICS, A., and MARK, H. J. Am. Chem. Soc. 64 : 1557. 1942.
3. ALFREY, T., JR., JUSTICE, D., and NELSON, S. Trans. Faraday Soc. (In press.)
4. CRAGG, L. H. J. Colloid Sci. 1 : 261. 1946.
5. CRAGG, L. H., ROGERS, T. M., and HENDERSON, D. A. Can. J. Research, B, 25 : 333. 1947.
6. FLORY, P. J. J. Chem. Phys. 10 : 51. 1942.
7. HOLMES, H. N. and BEEMAN, N. Ind. Eng. Chem. 26 : 172. 1934.
8. LOUNSBURY, K. B. Sc. Thesis, McMaster University. 1947.
9. RICE, F. A. H. Can. J. Research, B, 24 : 12. 1946.
10. ROGERS, T. M., HENDERSON, D. A., and CRAGG, L. H. Can. J. Research, B, 25 : 351. 1947.
11. SWITZER, D. F. Unpublished results, McMaster University.
12. WEISBERG, S. G. and SIMHA, R. J. Colloid Sci. 2 : 305. 1947.

THE STRUCTURE OF SOME DIELS–ALDER ADDITION PRODUCTS[1]

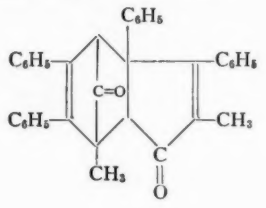
By H. L. Holmes, K. Alcock, D. G. Demianiw, J. W. Robinson, C. E. S. Rooney and F. A. Sundberg

Abstract

Six addition products have been prepared by the combination of various unsymmetrical dienes with unsymmetrical dienophiles (aldehydes and nitriles). Only one of the two possible adducts was isolated from each reactant pair. The structures of these adducts were established by their dehydrogenation to various known substituted benzaldehydes and benzoic acids. The results of this work are in complete agreement with the conclusion of Hudson and Robinson that the reaction of a diene with a dienophile involves the union of the anionoid end of the diene with the cationoid carbon of the dienophile.

Introduction

The bimolecular product resulting from the action of acid dehydrating agents upon α-methylanhydroacetonebenzil is a Diels–Alder adduct where the primary dehydration product fulfils the role both of diene and dienophile. Moreover the dissociation of this adduct into its components (in this case into the monomeric form) differs from the dissociation of other adducts only in degree rather than in kind. The dissymmetry of the monomer leads to four possibilities for the structure of the dimer. From degradative experiments Allen and Van Allan (4) concluded that "the preferred structure for the dimer is that shown in 1." One phase of this degradation involved the conversion



I

of the dimer to a triphenyltoluene identical with that derived from the monomer and phenylacetylene (obtained also from the adduct from the dehydrated α-methylanhydroacetonebenzil and phenylpropiolic acid by decarboxylation). Because of the unsymmetrical nature of the reactants, it has not been possible to unequivocally assign a structure to this triphenyltoluene. Acceptance of I for the bimolecular product of necessity requires that 2,3,5-triphenyltoluene is the adduct resulting from the action of phenylacetylene or phenylpropiolic acid upon the monomeric anhydro product.

[1] *Manuscript received in original form April 21, 1947, and as revised November 22, 1947.*

Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask., based on work completed in partial fulfilment of the requirements for a third year undergraduate course in Organic Chemistry.

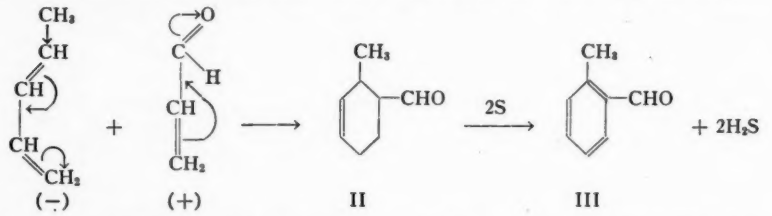
Conversely, any evidence substantiating the above structure for this substituted toluene would strengthen the argument in favor of I for the bimolecular product from dehydrated α-methylanhydroacetonebenzil.

The hypothesis of Hudson and Robinson (19, 25) for the orientation of the reactants (dienes and dienophiles) prior to combination offers a plausible explanation for the isolation of but one of the two possible adducts from various pairs of unsymmetrical addends (dienes and dienophiles) under normal conditions. Furthermore, this orientation of the two addends in a position permitting the combination of the anionoid end of the diene with the cationoid carbon of the dienophile offers attractive possibilities in choosing one of two possible structures for this adduct. However, before such a hypothesis can be applied with impunity to a problem such as that already cited it must be demonstrated that it holds for a goodly number of cases.

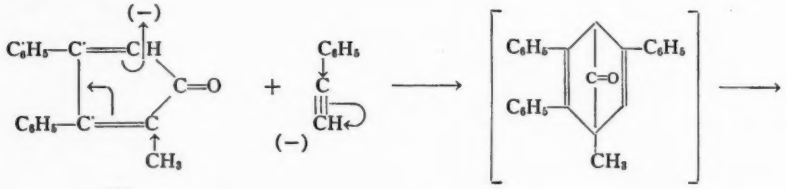
In most instances only one adduct is formed in the Diels–Alder reaction. However, when two adducts are formed this may be due to a shift of the newly generated double bond into a position of conjugation with some other center of unsaturation (9, 17) (β-benzoylacrylic acid + 2,3-dimethylbutadiene (14), benzalacetophenone + bicyclohexenyl (9), dibenzoylethylene + bicyclohexenyl (9), and ethyl cinnamate + bicyclohexenyl (28) or when both reactants are unsymmetrical (acrolein + 1,1,3-trimethylbutadiene (23) and 2,6-dimethoxy-4-*n*-amylcinnamic acid + isoprene (1)), these adducts may result from the orientation of the reactants in the two alternative arrangements prior to addition. Considering the number of combinations of unsymmetrical reactants that have been examined and found to yield a single adduct (quinones and substituted maleic anhydrides excepted) it is surprising that the structures of but seven of these adducts (acrolein + 1-phenylbutadiene-1,3 (21), acrolein + 2-ethoxy- and 2-methoxybutadiene-1,3 (15), 2,6-dimethoxy-4-*n*-amylcinnamic acid + isoprene (1), methyl 3,4-dihydro-1-naphthoate + 2-ethoxybutadiene-1,3 (18) and derivatives of sorbic acid with acrylyl chloride (27) and vinylphenylketone (3)) have been rigorously established. Since the structure of such a limited number of adducts from unsymmetrical addends has been clearly established, it is not yet possible to satisfactorily evaluate the relative effects of the various factors obtaining in this reaction and from them to derive a method for predicting the structure of an adduct resulting from a given pair of reactants. It is with this in view that six other adducts have been prepared from unsymmetrical reagents and the structure of five of these established.

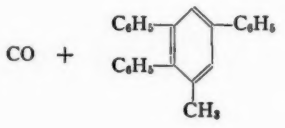
The various Diels–Alder addition products were obtained by heating equimolar quantities of the two addends (see Table I) in a sealed tube at 145° to 150° C. (a temperature of 170° C. was used in the combination of crotonaldehyde with 1-methylbutadiene and with 1,3-dimethylbutadiene) for 24 hr. Under these conditions the reactions were far from quantitative (some starting material and a considerable amount of polymeric material was formed in each case), however, only one addition product was recovered from each reactant pair. The structures of the aldehydic adducts were established

(*a*) by dehydrogenation to, and characterization of, the respective substituted benzaldehydes (for example, 2-methyl-Δ^3-tetrahydrobenzaldehyde, II, ——→ *o*-methylbenzaldehyde, III) and (*b*) by oxidation of the aldehydic adduct*



with silver oxide (15) to the respective acid, followed by dehydrogenation to, and the characterization of, the respective benzoic acids (see Table II). In the case of the acrylonitrile-1-methylbutadiene adduct the structure was established (*a*) by dehydrogenation to *o*-methylbenzonitrile followed by hydrolysis to *o*-methylbenzoic acid and (*b*) by alkaline hydrolysis of the adduct to the respective acid** followed by dehydrogenation to *o*-methylbenzoic acid. The acid resulting from the oxidation of the crotonaldehyde–isoprene adduct (m.p. 60° to 62° C.), although it was somewhat waxy in nature, appeared to be different from the acid (m.p. 81° to 83° C.) derived from the addition of crotonic acid to isoprene (23). A similar pair of isomeric acids have been obtained in an analogous way from the addition of acrolein and acrylic acid to 1-phenylbutadiene (21). An investigation of the acids from acrolein and acrylic acid with isoprene is planned for a later date. The results of this work combined with that already reported in the literature, while still limited in scope, indicate that the hypothesis of Hudson and Robinson obtains in all the cases studied. As might be expected the resonance effect of the carboxyl group of crotonaldehyde exerts a greater influence than the inductive effect of the methyl group.





* *The crotonaldehyde-1,3-dimethylbutadiene adduct was resistant to oxidation by this reagent.*

** *This acid proved to be identical with that from the oxidation of the acrolein–piperylene adduct (see Table I).*

Returning now to the monomeric form (IV) of dehydrated α-methylanhydroacetonebenzil, examination will disclose that the dissymmetry of the molecule stems from the C-methyl group and it is to be expected that the inductive effect of this grouping would cause an orientation in such a fashion that it would combine with phenylacetylene to give 2,3,5-triphenyltoluene (V).

Experimental*

2-Methyl-Δ^3-tetrahydrobenzaldehyde

A mixture of 24.8 gm. of acrolein and 30.0 gm. of redistilled piperylene (b.p. 40° to 40.5° C. (707 mm.)) was heated in sealed tubes at 145° to 150° C. for 24 hr. The reaction product was heated to 70° C. to remove any unchanged starting material and the remaining oil was distilled up to 80° C. (25 mm.) (27.3 gm.). Redistillation of the oily adduct gave 21.8 gm. (39.8% of 2-methyl-Δ^3-tetrahydrobenzaldehyde which boiled constantly at 73° to 75° C. (25 mm.) and had a refractive index, $n_D^{25} = 1.4665$ (see Table I for the yields and physical constants of the other adducts).

The 2,4-dinitrophenylhydrazone crystallized from ethanol in long silky orange needles and melted at 141° to 142° C. Calc. for $C_{14}H_{16}O_4N_4$: N, 18.41%. Found: N, 18.25, 18.82%.

Oxidation of the Acrolein-1,3-dimethylbutadiene Adduct

The aldehydic adducts, with the exception of the crotonaldehyde-1,3-dimethylbutadiene adduct, were oxidized to the respective acids with aqueous silver oxide (15). A vigorously stirred suspension of 9.0 gm. of the acrolein-1,3-dimethylbutadiene adduct in a solution of 53.0 gm. of silver nitrate in 80 cc. of water and 16 cc. of ethanol, cooled to 0° C., was made alkaline by the addition of a solution of 29.0 gm. of potassium hydroxide in 80 cc. of water. The reaction mixture was stirred at this temperature for one hour and finally for 30 min. at room temperature. The suspended solid material was collected on a Büchner funnel and washed with water. The filtrate was made acid to litmus with dilute sulphuric acid and the oily acid recovered by six extractions with ether. The ethereal solution was washed with water and dried over anhydrous sodium sulphate. After removal of the solvent 6.7 gm. (67%) of the oily acid distilled at 149° to 150° C. (24 mm.). The distillate solidified in the receiver and after redistillation it melted at 60° to 62° C. and crystallized from aqueous methanol it melted at 75° to 76° C.

All the acids of this type decolorized a carbon tetrachloride solution of bromine. The yields and physical constants of these acids are recorded in Table I.

Hydrolysis of 2-Methyl-Δ^3-tetrahydrobenzonitrile

A suspension of 5.3 gm. of the acrylonitrile–piperylene adduct in 40 cc. of 15% aqueous sodium hydroxide solution was boiled for 20 hr. The alkaline

** All melting points were taken in an apparatus designed by E. B. Hershberg, Ind. Eng. Chem., Anal. Ed. 8 : 312. 1936, and are corrected unless otherwise stated. All compounds were analyzed in the analytical laboratories of Dr. Léo Marion, National Research Council, Ottawa, Canada, and of A. Ledingham, Dominion Rubber Research Laboratory, Guelph, Ontario.*

TABLE I

PHYSICAL CONSTANTS OF SOME DIELS–ALDER ADDUCTS AND THEIR RESPECTIVE ACIDS

	Yield, %	Boiling point, °C.	n_D^{25}	B.p. and m.p. of acid, °C.	Yield, %	n_D^{25}
ACROLEIN						
(1) 1-methylbutadiene-1,3 (5)	39.8	73–75 (25 mm.)	1.4665	141 (20 mm.)	79	1.4675
(2) 1,3-dimethylbutadiene-1,3 (13)	50	94–96 (30 mm.)[a]	1.4696	149–150 (24 mm.) 75–76	67	—
ACRYLONITRILE						
(3) 1-methylbutadiene-1,3[b]	35	94–96 (24 mm.)	1.4609	140–141 (20 mm.)	52	1.4678[c]
CROTONALDEHYDE						
(4) 1-methylbutadiene-1,3	52	80–81 (20 mm.)	1.4686	143 (22 mm.) 66–67	45	—
(5) 2-methylbutadiene-1,3 (13, 23)	50	96–98 (27 mm.)	1.4686	154–156 (20 mm.)[d] 60–62	47	—
(6) 1,3-dimethylbutadiene-1,3 (23)	74	94–95 (23mm.)[e]	1.4679	—	0[f]	—

[a] *The semicarbazone, after repeated crystallization and drying at 100° C. (20 mm.), melted at 134° C. The figure quoted in the literature (13) is 174° C. Calc. for* $C_{10}H_{17}ON_3$*: N, 21.53%. Found: N, 21.28, 21.09%.*

[b] *Calc. for* $C_5H_{11}N$*: N, 11.55%. Found: N, 11.54, 11.61%.*

[c] *This acid is identical with that derived from the acrolein-1-methylbutadiene adduct. The amide melts alone or on admixture with that from the alternate method of preparation at 147° to 149° C.*

[d] *This acid appears to be different from that of the addition of isoprene to crotonic acid (m.p. 81° to 83° C.). The amide of this acid melts at 154° to 155° C.*

[e] *The semicarbazone melts at 184.5° to 185° C.*

[f] *The aldehyde was recovered unchanged after treatment with aqueous silver oxide.*

solution was extracted with ether to remove any nitrile. The aqueous solution was acidified and extracted many times with ether, and the extract washed with water and dried over anhydrous sodium sulphate. After removal of the solvent the oily acid (3.2 gm.; 52%) distilled at 139° to 141° C. (20 mm.) and had $n_D^{20} = 1.4678$. The acid from the oxidation of the acrolein–piperylene adduct boiled at 140° to 141° C. (20 mm.) and had $n_D^{25} = 1.4675$. The amide from the hydrolyzed product melted at 147° to 149° C. and showed no depression when mixed with that derived from the acrolein–piperylene adduct.

Dehydrogenation

(*a*) *Aldehydes*

A typical example of the procedure used in all cases is that of the dehydrogenation of the acrolein-1,3-dimethylbutadiene adduct. A mixture of 6.8 gm. of the adduct and 3.32 gm. of sulphur (5% excess) was heated in a von Braun flask to 280° C. for 15 min., then the distillate in the receiver was transferred to a small distilling flask and the fraction (1.7 gm.; 28%) boiling at 212° to 215° C. (710 mm.) was collected. The semicarbazone crystallized in light fluffy crystals from dilute acetic acid and melted at 227° to 228° C. (uncorr.). The results of the dehydrogenation of the various aldehydic adducts and the physical constants of the substituted benzaldehydes and their derivatives are recorded in Table II.

TABLE II

PHYSICAL CONSTANTS OF THE PRODUCTS OF DEHYDROGENATION OF THE ACID AND ALDEHYDE ADDUCTS

Dehydrogenation product of—	B.p. or m.p., °C.	M.p. of derivative, °C.	Product cited from the literature	B.p. or m.p., °C.	M.p. of derivative, °C.
Adduct No. 1	195–197 (710 mm.)	S-212[a]	*o*-Methylbenzaldehyde	199–200 (760 mm.) (11)	S-212 (10)
Adduct No. 2	212–215 (710 mm.)	S-227–228	2,4-Dimethylbenzaldehyde	216–218 (760 mm.) (16)	S-225–227 (6)
Adduct No. 3	204–205 (710 mm.)	—	*o*-Methylbenzonitrile	205 (760 mm.) (24)	—
Adduct No. 4	223–226 (712 mm.)	S-157–158	2,6-Dimethylbenzaldehyde	226–228 (741 mm.) (22)	S-158 (22)
Adduct No. 6	232–235 (714 mm.)	O-181–182[b]	2,4,6-Trimethylbenzaldehyde	237 (760 mm.)	O-179-181 (26)
Acid of adduct No. 1	99–101	A-137–138[c]	2-Methylbenzoic acid	105.5 (7)	A-140 (20)
Acid of adduct No. 2	124.5–126	A-181–182	2,4-Dimethylbenzoic acid	126 (8)	A-179–181 (2)
Acid of adduct No. 3	100–100.5	A-137–138	2-Methylbenzoic acid	105.5 (7)	A-140 (20)

[a] *The letter 'S' indicates that the derivative quoted is the semicarbazone.*
[b] *The letter 'O' indicates that the derivative quoted is the oxime.*
[c] *The letter 'A' indicates that the derivative quoted is the amide.*

(*b*) *Acids*

A typical example of the dehydrogenation of the acid-adducts is as follows. A mixture of 2.75 gm. of 2,4-dimethyl-Δ^3-tetrahydrobenzoic acid and 1.34 gm. of sulphur (5% excess) in a von Braun flask was heated in a salt bath at 240° to 245° C. for 40 min. and the temperature finally raised to 270° C. for 10 min. The volatile material was distilled at 2 mm. and the semisolid distillate dissolved out of the receiver with ether. Removal of the ether and crystallization of the residue from water gave 0.3 gm. of yellow needles, melting at 115° to 120° C. Recrystallization of this dehydrogenated acid from petroleum ether (b.p. 30° to 60° C.) raised the melting point to 124.5° to 126° C. The amide, once recrystallized from water, melted at 181° to 182° C. The results of the dehydrogenation of the other acid-adducts will be found in Table II.

(*c*) *Nitriles*

The acrylonitrile–piperylene adduct was dehydrogenated by heating 3.0 gm. of the addition product to 240° to 260° C. for one hour with 1.66 gm. of sulphur. The reaction product was distilled (b.p. 203° to 205° C. (710 mm.)). The oily distillate was redistilled and the fraction (0.5 gm.) boiling at 204° to 205° C. (710 mm.) was collected; it had $n_D^{25} = 1.5205$. *o*-Methylbenzonitrile boils at 205° C. (24) and has $n_D^{25} = 1.5272$ (12).

The *o*-methylbenzonitrile (0.4 gm.) was hydrolyzed by boiling with 25 cc. of 15% sodium hydroxide solution for 20 hr. The alkaline solution was filtered, extracted with ether and acidified. The *o*-toluic acid was extracted from the aqueous solution with ether, and the extract washed with water and dried over anhydrous sodium sulphate. Removal of the solvent left a straw-colored oil which soon solidified. Crystallization of this crude product from petroleum ether (b.p. 30° to 60° C.) gave a crystalline solid which melted alone or on admixture with the *o*-toluic acid from the dehydrogenation of 2-methyl-Δ^3-tetrahydrobenzoic acid at 100° to 100.5° C.

The amide, once crystallized from water, melted at 137° to 138° C.

Acknowledgment

A generous supply of 2-methylpentadiene-1,3 was received from Shell Development Company, Emeryville, California. This gift is gratefully acknowledged.

References

1. ADAMS, R. and CARLIN, R. B. J. Am. Chem. Soc. 65 : 360. 1943.
2. ADOR, E. and MEIER, F. Ber. 12 : 1968. 1879.
3. ALLEN, C. F. H., BELL, A. C., BELL, A., and VAN ALLAN, J. J. Am. Chem. Soc. 62 : 656. 1940.
4. ALLEN, C. F. H. and VAN ALLAN, J. J. Org. Chem. 10 : 333. 1945.
5. ARBUZOV, B., Zinov'eva, Z., and Fink, I. J. Gen. Chem. (U.S.S.R.), 7 : 2278. 1937. *Abstracted in* Chem. Abstracts 32 : 507. 1938.
6. AUWERS, K. and HESSENLAND, M. Ann. 352 : 273. 1907.
7. AUWERS, K. and ROTH, W. A. Ann. 373 : 239. 1910.

8. BENTLEY, W. H. and PERKIN, W. H. J. Chem. Soc. 71 : 157. 1897.
9. BERGMANN, F. and ESCHINAZI, H. E. J. Am. Chem. Soc. 65 : 1405. 1943.
10. BLAISE, E. E. and COURTOT, A. Bull. soc. chim. [3] 35 : 373. 1906.
11. BORNEMANN, E. Ber. 17 : 1462. 1884.
12. BRÜHL, J. W. Z. physik. Chem. 16 : 218. 1865.
13. DIELS, O. and ALDER, K. Ann. 470 : 62. 1929.
14. FIESER, L. F. and FIESER, M. J. Am. Chem. Soc. 57 : 1679. 1935.
15. FIESSELMANN, H. Ber. 75 : 881. 1942.
16. GATTERMANN, L. Ann. 347 : 347. 1906.
17. HOLMES, H. L., HUSBAND, R. M., LEE, C. C., and KAWULKA, P. J. Am. Chem. Soc. 70 : 141. 1948.
18. HOLMES, H. L. and MANN, K. M. J. Am. Chem. Soc. 69 : 2000. 1947.
19. HUDSON, B. J. F. and ROBINSON, SIR R. J. Chem. Soc. 715. 1941.
20. HUTCHINSON, A. Ber. 24 : 173. 1891.
21. LEHMANN, E. and PAASCHE, W. Ber. 68 : 1146. 1935.
22. LOCK, G. and SCHMIDT, K. J. prakt. Chem. 140 : 229. 1934.
23. M. NAEF & CIE. Fr. Patent 672,025. March 25, 1929.
24. PERKIN, W. H. J. Chem. Soc. 69 : 1025. 1896.
25. PRICE, C. C. Reactions at carbon-carbon double bonds. John Wiley & Sons, Inc., New York. 1946.
26. SCHOLL, R. and KAVER, F. Ber. 36 : 322. 1903.
27. WAGNER-JAUREGG, T. and HELMERT, E. Ber. 71 : 2535. 1938.
28. WEIZMANN, C., BERGMANN, E., and BERLIN, T. J. Am. Chem. Soc. 60 : 1331. 1938.

CANADIAN JOURNAL OF RESEARCH

Notes on the Preparation of Copy

GENERAL:—Manuscripts should be typewritten, double spaced, and the **original and one extra copy** submitted. Style, arrangement, spelling, and abbreviations should conform to the usage of this Journal. Names of all simple compounds, rather than their formulae, should be used in the text. Greek letters or unusual signs should be written plainly or explained by marginal notes. Superscripts and subscripts must be legible and carefully placed. Manuscripts should be carefully checked before being submitted, to reduce the need for changes after the type has been set. If authors require changes to be made after the type is set, they will be charged for changes that are considered to be excessive. **All pages, whether text, figures, or tables, should be numbered.**

ABSTRACT:—**An abstract of not more than about 200 words, indicating the scope of the work and the principal findings, is required.**

ILLUSTRATIONS:

(i) *Line Drawings:*—All lines should be of sufficient thickness to reproduce well. Drawings should be carefully made with India ink on white drawing paper, blue tracing linen, or co-ordinate paper **ruled in blue only**; any co-ordinate lines that are to appear in the reproduction should be ruled in black ink. Paper ruled in **green, yellow, or red should not be used** unless it is desired to have all the co-ordinate lines show. Lettering and numerals should be neatly done in India ink preferably with a stencil (**do not use typewriting**) and be of such size that they will be legible and not less than one millimetre in height when reproduced in a cut three inches wide. All experimental points should be carefully drawn with instruments. Illustrations need not be more than two or three times the size of the desired reproduction, but the ratio of height to width should conform with that of the type page. **The original drawings and one set of small but clear photographic copies are to be submitted.**

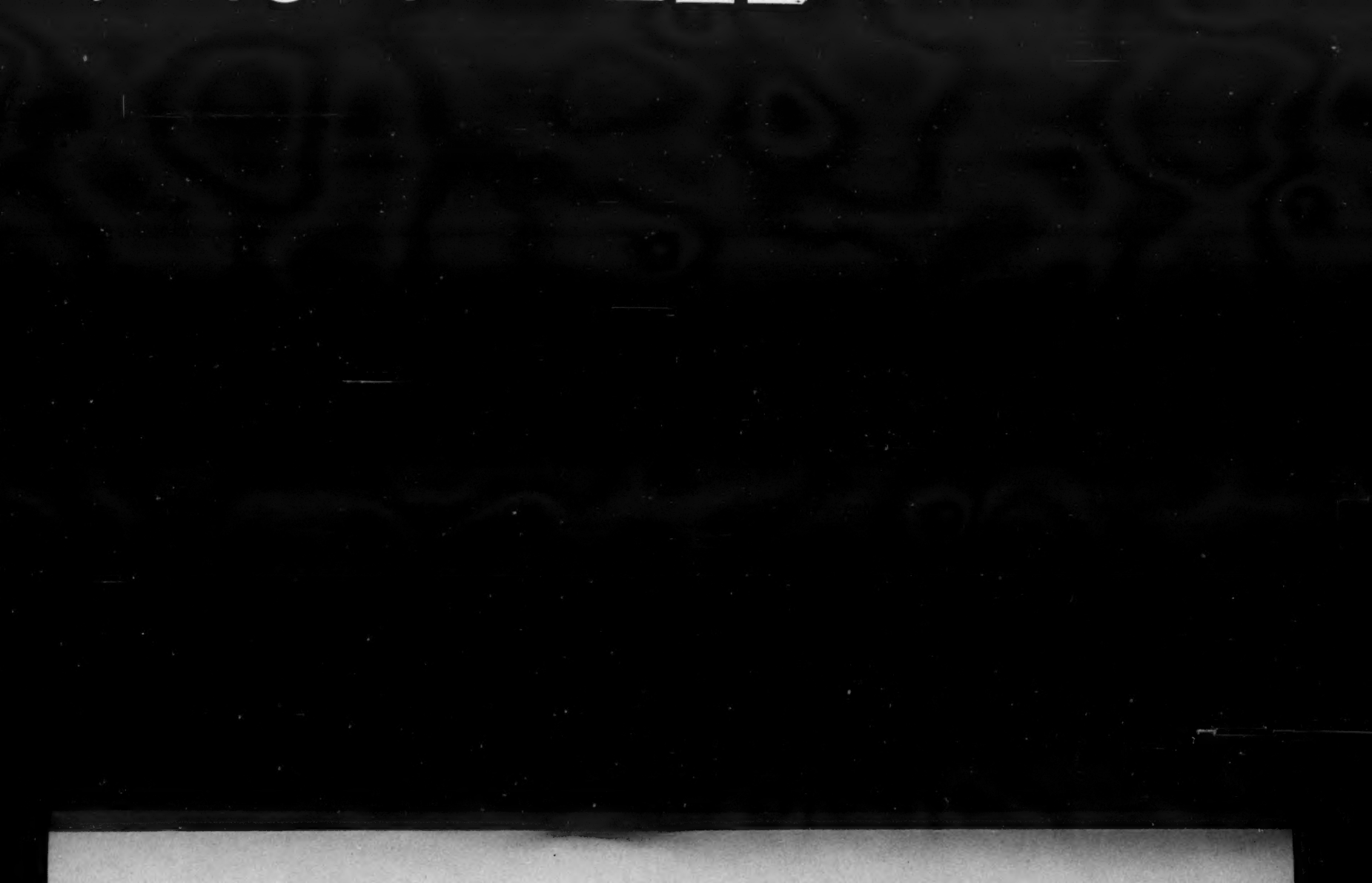
(ii) *Photographs:*—Prints should be made on glossy paper, with strong contrasts; they should be trimmed to remove all extraneous material so that essential features only are shown. Photographs should be submitted **in duplicate**; if they are to be reproduced in groups, one set should be so arranged and mounted on cardboard with rubber cement; the duplicate set should be unmounted.

(iii) *General:*—**The author's name, title of paper, and figure number should be written in the lower left hand corner (outside the illustration proper) of the sheets on which the illustrations appear.** Captions should not be written on the illustrations, but typed on a separate page of the manuscript. All figures (including each figure of the plates) should be numbered consecutively from 1 up (arabic numerals). **Each figure should be referred to in the text.** If authors desire to alter a cut, they will be charged for the new cut.

TABLES:—Titles should be given for all tables, which should be numbered in Roman numerals. Column heads should be brief and textual matter in tables confined to a minimum. **Each table should be referred to in the text.**

REFERENCES:—**These should be listed alphabetically by authors' names, numbered in that order, and placed at the end of the paper.** The form of literature citation should be that used in the respective sections of this Journal. **Titles of papers should not be given in references listed in Sections A, B, E, and F, but must be given in references listed in Sections C and D.** The first page only of the references cited in papers appearing in Sections A, B, and E should be given. **All citations should be checked with the original articles.** Each citation should be referred to in the text by means of the key number; in Sections C and D the author's name and the date of publication may be included with the key number if desired.

The *Canadian Journal of Research* conforms in general with the practice outlined in the *Canadian Government Editorial Style Manual*, published by the Department of Public Printing and Stationery, Ottawa.

Reprints

Fifty reprints of each paper without covers are supplied free. Additional reprints, if required, will be supplied according to a prescribed schedule of charges. On request, covers can be furnished at cost.